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PERFORMANCE TESTING OF METHOD 1312

QA SUPPORT FOR RCRA TESTING: PROJECT REPORT

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16. ABSTRACT

The question of how to access the risks associated with ground water contamination from soils containing toxic substances is a critical issue for the Agency. A major limitation of using Method 1310 and 1311 for this purpose is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants (specifically lead) and incorrectly classify the solid as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment. The EPA is considering the use of a newly created synthetic acid precipitation leach test for soils (Method 1312) to provide information about the mobility (leachability) of both organic and inorganic contaminants present in soils. This new test method is similar to the TCLP (Method 1311) except that the initial liquid solid separation step has been eliminated and the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. This acid mixture simulates the nature of the precipitation occurring in the region where the soil sample originated. This report presents the satisfactory results obtained from precision evaluation of and ruggedness test for Method 1312. Several different soils were fortified with semi-volatile organics, metal salts and volatile organics, and then leached in replicate to determine method precision. A ruggedness evaluation was performed by making minor changes in specified method values to identify procedural variations requiring careful control.

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ABSTRACT

The question of how to access the risks associated with ground water contamination from soils containing toxic substances or wastes disposed of in a monofill environment is a critical issue for the Agency. A major limitation of using Methods 1310 and 1311 for this purpose is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils or wastes disposed of in a monofill environment. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants (specifically lead) and incorrectly classify the soil or waste as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment. The EPA is considering the use of a newly-created synthetic acid precipitation leach test for soils and wastes (Method 1312) to provide information about the mobility (leachability) of both organic and inorganic contaminants present in these materials. This new test method is similar to the TCLP (Method 1311) except that the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. This acid mixture simulates the nature of the precipitation occurring in the region where the soil sample originated. A pH 4.2 acid precipitation solution is used for extraction of wastes.

The purpose of this report is to present results obtained from a precision evaluation of and ruggedness test for Method 1312 for soils only. Several different soils were fortified with semi-volatile organics, metal salts and volatile organics, and then leached in replicates of 3 or 6 to determine method precision. A ruggedness evaluation was performed by making minor changes in specified method values to identify procedural variations requiring careful control.

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INTRODUCTION

This report summarizes the quality assurance support provided to the Office of Solid Waste in FY-88 by the Quality Assurance and Methods Development Division, Environmental Monitoring Systems Laboratory - Las Vegas, Office of Research and Development, under D109 Q01, "QA Support for RCRA." The major activity conducted by the EMSL-LV under D109 Q01 was the evaluation of EPA Method 1312, a proposed synthetic acid precipitation leach test for soils and wastes.

Section 3001 of the Resource Conservation and Recovery Act (RCRA)[1] mandated that the U.S. Environmental Protection Agency (EPA) identify those wastes which pose a hazard to human health and the environment if improperly managed, e.g., disposal in an unsecured sanitary landfill. The EPA initially specified that the Extraction Procedure (EP) Toxicity Characteristic,[2] Method 1310, be used to identify wastes which pose a probable hazard due to their potential to leach significant amounts of 14 specific toxic species (8 metals, 4 insecticides and 2 herbicides). The EP required that the sample be leached for 24 hours and required repetitive sample pH adjustment to 5.0 ± 0.2 with dilute acetic acid. Method 1310 was optimized to evaluate the leaching of elemental (inorganic) rather than organic constituents and to provide a reproducible (precise) test method.

In an effort to eliminate operational problems of the EP protocol and to increase its applicability to additional toxic constituents that could leach from hazardous waste in landfills, the EPA proposed Method 1311, Toxicity Characteristic Leaching Procedure (TCLP). Method 1311 expanded the list of EP analytes to include 38 additional organic compounds and introduced an improved leaching technique suitable for evaluating wastes containing both organic and inorganic toxicants. Method 1311 requires separate leaching procedures for (1) volatile organic and (2) semi-volatile organic or inorganic analytes using an acetate buffer with a pH appropriate for the alkalinity of the waste being characterized. A glass extraction vessel is employed for the leaching of semi-volatile organics and metals. Volatile organic analytes require a specialized extraction vessel, the zero-headspace extractor (ZHE). The sample is filtered and then leached for 18 hours in a rotary tumbler. The resulting aqueous leachate is analyzed by appropriate SW-846 methods. A copy of the Method 1311 procedure is included in Appendix D.

The specific mismanagement scenario modeled by the TCLP is co-disposal of industrial waste with municipal refuse in a sanitary landfill. The leaching procedure is intended to simulate the leaching action of low molecular weight organic acids generated in an actively decomposing sanitary landfill. The leaching test is used to predict whether ground water contamination could result from improper waste management due to the migration (leaching) of toxic species from the disposal site. The EPA considers the TCLP to be adequate in terms of indicating the potential for wastes to pose a hazard if mismanaged,[3] and has subjected the test to precision[4,5] and ruggedness[6,7] evaluations in addition to several multi-laboratory validation studies(8-10).

The question of how to assess the risks associated with ground water contamination from soils containing toxic substances or wastes disposed of in a monofill environment is also a critical issue for the EPA. The large number of samples needing analysis under legislative mandate requires that a leaching procedure be rapid, accurate, reproducible, rugged, and suitable for a variety of matrices. A major limitation of using Methods 1310 and 1311 for this purpose is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils or wastes disposed of in a monofill environment. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants (specifically lead) and incorrectly classify the soil or waste as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment. The EPA is considering the use of a newly-created synthetic acid precipitation leach test for soils and wastes (Method 1312) to provide information about the mobility (leachability) of both organic and inorganic contaminants present in these matrices. This new test method is similar to the TCLP (Method 1311) except that the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. This acid mixture is either pH 4.2 or 5.0, which simulates the nature of the precipitation occurring where the soil sample originated. A pH 4.2 acid precipitation solution is used for extraction of wastes. A copy of the Method 1312 procedure is included in Appendix C.

The purpose of this report is to present results obtained from a precision evaluation of and ruggedness test for Method 1312 for soils only. Several different soils were fortified with semi-volatile organic compounds, metal salts and volatile organic compounds, and then leached in replicates of 3 or 6 analyses to determine method precision. Minor changes were made in specified method values, and a ruggedness evaluation was performed to identify procedural variations requiring careful control.

CONCLUSION

Method 1312 is a reasonably rugged and precise method that can be used to address the mobility of pollutants in soil samples. The performance of Method 1312 for leaching organic compounds was very similar to that of Method 1311 (TCLP). Method 1312 was less efficient at leaching cadmium and lead than was Method 1311.

RECOMMENDATIONS

Method 1312 is suitable for the characterization of soil samples. However, additional information on the performance of the method as a model for the mobility of toxicants in the environment is required. It is recommended that studies be conducted to: measure the mobility of different lead- and mercury-containing compounds in the soil; compare the mobility of toxicants in soil columns with Method 1312 mobility; and develop sepcific performance data for SW-846 methods (i.e., Method 8150 and Method 8081) when they are used to analyze Method 1312 leachates.

EXPERIMENTAL DESIGN

The evaluation of the precision and ruggedness of the Method 1312 protocol was conducted as two different studies. One tested the procedure for volatiles and required the use of a ZHE for leaching studies. The other tested the procedure for semi-volatile organic compounds and inorganic analytes (extractable analytes). The experimental designs and analytical procedures used for these two evaluations of the Method 1312 protocol are summarized below.

EXTRACTABLE COMPOUNDS PROCEDURE

Two different types of clean soil were used in the single laboratory (EMSL-LV, LESC) precision and ruggedness evaluation of the Method 1312 protocol: an eastern soil with high organic content and a western soil with low organic content (sandy type). Both soils were analyzed prior to fortification to ensure that they contained no significant concentrations of organics or metals that might complicate sample analysis and/or data interpretation. Analytes were selected for fortification in order to represent the range of analyte volatility, polarity, acidity-basicity, and compatibility (chemical reactivity) of the compounds on the TCLP target compound list. Analyte spiking levels were carefully selected so that expected analyte concentrations in the soil leachate would be close to TCLP regulatory levels. Refer to Table 2 for the amount of each extractable compound typically spiked into 100 grams of soil.

An appropriate amount of spiking solution containing the semi-volatile analytes was added to 100 g of soil. The soil and spiking solution were thoroughly mixed and stored at 4° C for at least 15 hours. The sample was then wetted by adding 50 ml of water containing appropriate amounts of metals (lead and cadmium). This mixture was allowed to equilibrate at 4° C for at least 15 hours prior to application of the leaching procedure. The aqueous soil leachate was filtered, extracted with methylene chloride (Method 3520 continuous liquid-liquid extraction), concentrated, and analyzed for semi-volatiles by gas chromatography/mass spectrometry (GC/MS, Method 8270). The aqueous soil leachate was analyzed directly for metals by inductively coupled plasma/mass spectrometry (ICP/MS, draft Method 6020).

Triplicate aliquots of the eastern soil were leached using four different extraction fluids (pH 3.2, 4.0, 5.0, 6.1) to determine if the pH of the leaching fluid has a significant effect on either method precision or recovery. Triplicate aliquots of the western soil were spiked at two different analyte concentration levels, leached, and analyzed to obtain data on the matrix sensitivity of the method as well as its dynamic range. Information about the sensitivity of the western soil to the pH of the leaching fluid was obtained during the ruggedness test described below.

A ruggedness evaluation was designed to determine the sensitivity of Method 1312 to modest departures from the leaching protocol which can be expected during routine application of the protocol. In this way, procedural variations that must be carefully controlled and the limits of acceptable deviation with respect to these variables could be identified. The ruggedness evaluation of Method 1312 for both volatile and non-volatile species was performed by following the test procedure of Youden and Steiner[11] (Statistical Manual of the AOAC, 1975) which is designed to determine the level of significance for seven variables using just eight different measurements. For the semi-volatile compounds and the metals, the western soil was used for the ruggedness evaluation. The experimental parameters chosen for evaluation were: (1) leaching fluid pH, (2) liquid/solid ratio, (3) extraction time, (4) particle size reduction, (5) type of extractor vessel, (6) number of filters used, and (7) temperature. Refer to Table 4 for the specific procedural modifications used in the ruggedness test.

VOLATILES PROCEDURE

The single laboratory precision and ruggedness evaluation of Method 1312 for the volatile organic compounds was performed by Acurex and Midwest Research Institute (MRI) as a single parallel laboratory study. Two contaminated soils originating in the western (Soil 1) and eastern (Soil 2) U.S. from Superfund sites and two soils prepared by combining a clean soil from Hayward, California with two different municipal sludges in the laboratory (identified as California Urban Soils 3 and 4) were used for the precision evaluation of Method 1312. These soil samples were analyzed to measure organic and inorganic contaminants for safety purposes and to establish appropriate spiking levels for the fortification mixture containing 27 Method 1312 volatile target analytes. (The initial characterization results for these samples are presented in Appendix B).

Soil 1 (western soil) and Soil 2 (eastern soil) were air dried overnight in a fume hood prior to their use. An aliquot of 25 grams of the dried soil was placed into a ZHE and distributed evenly over the top of the piston and then spiked with the volatile compound fortification solution. The filter assembly was put in place immediately and the device was sealed as rapidly as possible. The appropriate leaching fluid (pH 4.2 or 5.0) was added to the ZHE which was then rotated for 16 hours. After this period, the soil leachate was collected in a 50 ml gastight syringe; the leachate was transferred to precleaned VOA vials with no headspace. These vials were stored at 4° C until analysis by capillary GC/MS (Method 8260). Soils 1 and 2 were prepared and analyzed in triplicate to obtain precision data for Methods 1312/8260 on real-world contaminated soils.

The California Model Urban Soils (Soils 3 and 4) were prepared by separately mixing clean Hayward, California soil (dried overnight at 120° C) with two municipal sludges from San Francisco Bay area sites. They were prepared to simulate a worst case soil that might be tested by Method 1312. Aliquots of 25 grams of Soils 3 and 4 were placed into a ZHE, then spiked directly with the ZHE piston up using 240 µL of fortification solution containing 200 µg/mL of 27 volatile analytes (Table 3). The ZHE was assembled as quickly as possible and then was placed in a refrigerator at 4° C for 1 hour prior to the addition of leaching fluid. Following this equilibration period, the sample was leached. The soil leachate was transferred to an evacuated Tedlar bag. Each bag was used to fill several VOA vials. These vials were capped and then immediately stored at 4° C until they were analyzed. The leachate was analyzed for volatile compounds by GC/MS (Method 8260). Soils 3 and 4 were leached in replicates of 6 analyses to obtain additional data to evaluate precision.

For the Method 1312 ruggedness test for volatile compounds using the ZHE, the following parameters were chosen for evaluation: (1) leaching fluid pH, (2) type of ZHE apparatus, (3) extraction time, (4) liquid/solid ratio, (5) particle size reduction, (6) buffer solution addition, and (7) soil analyte concentration. The clean Hayward, California soil was used in this study. Eight measurements were performed in the manner previously described for the extractable compounds. Refer to Tables 7 and 8 for the specific minor modifications of the leaching procedure used in the ruggedness test.

RESULTS AND DISCUSSION

EXTRACTABLE COMPOUNDS PRECISION

The precision of Method 1312 was evaluated by measuring the repeatability of recovery of 14 semi-volatile organic compounds, lead and cadmium. Table 1 summarizes the data for an eastern soil, and Table 2 summarizes that for a western soil. The recovery levels for individual replicate leachings used to calculate the average recoveries and %RSDs presented in Tables 1 and 2 are given in Appendix A. The recovery determinations were made by fortifying soil samples prior to using the leaching procedure. The reported variability is a combination of that from the leaching test (Method 1312) and that from the analytical methods (Methods 3250/8270 for organics and Method 6020 for inorganics). The variability of the organic analytical methods can be estimated from the RSDs (relative standard deviations) of the organic surrogates, thus, they are reported with the sample data. The organic surrogates added to the eastern soil leachate had recoveries greater than 60 percent and RSDs less than 9 percent while the recoveries for the semi-volatile analytes varied from 0.1 to 80 percent and the RSDs for analytes with reasonable recoveries generally ranged from 5 to 12 percent. The RSDs of the recoveries of most compounds reported in Table 1 are less than 10 percent. The precision of the Method 1312 recoveries for most compounds at all four pH values is similar to that of the GC/MS surrogates and is better than the precision obtained using Method 1311. Large (greater than 15 percent) RSDs were observed for four compounds. Three of these, 1,2-dichlorobenzene, 2,4-dimethylphenol, and 2,4-dinitrophenol, present analytical difficulties due to their volatility or reactivity. The fourth compound, hexachlorobenzene, had very low recovery and its very large RSD, in part, is the result of measurements made near the quantitation limit of Method 8270.

In general, semi-volatile analyte recoveries were lower and the RSDs were higher for the western soil than for the eastern soil. This appears to be related to the extraction and measurements steps since the RSDs of the organic surrogates added to the soil leachate were also higher for the western soil. The eastern (high organic content clay) and western (low organic content sand) soils are considerably different and thus the matrix sensitivity suggested is reasonable and is consistent with previous TCLP work. In Table 2 the surrogate RSDs vary from 7 to 63 percent and the semi-volatile analyte RSDs range from 6 to 55 percent for the western soil. Thus, the analytical variability of Methods 3520/8270 is comparable to the total variability of the leaching procedure. The precision data reported for the western soil is in general agreement with that of a prior precision evaluation of the TCLP (Method 1311) for extractable components.[5] In the TCLP precision study,

TABLE 1. METHOD 1312 PRECISION RESULTS FROM EASTERN SOIL

	Extraction Fluid pH								Method 1311	
	3.2		4.0		5.0		6.0			
	Avg. % Rec.	%RSD	Avg. % Rec.	%RSD	Avg. % Rec.	%RSD	Avg. % Rec.	%RSD	Avg. %Rec.	%RSD
FORTIFIED ANALYTES										
bis(2-chloroethyl)-ether	75.6	9.5	80.2	12.5	69.4	5.7	71.1	6.0	56.6	14.7
2-Chlorophenol	61.4	8.8	62.5	6.8	52.1	9.1	57.2	9.5	42.5	15.5
1,4-Dichlorobenzene	15.8	5.3	17.2	12.3	16.0	10.1	15.3	12.3	7.9	11.7
1,2-Dichlorobenzene	11.5	20.2	11.3	8.0	9.9	12.1	11.0	21.5	8.2	5.8
2-Methylphenol	47.6	9.9	47.3	7.7	40.4	7.6	43.5	12.6	40.8	14.4
Nitrobenzene	72.9	2.3	80.4	10.0	66.9	4.3	65.5	4.3	45.2	12.8
2,4-Dimethylphenol	12.3	9.1	13.7	18.4	8.4[b]	0.4	7.8	3.8	3.8	27.5
Hexachlorobutadiene	1.2	3.5	1.5	12.9	1.2	5.8	1.2	13.4	0.3	22.4
Acenaphthene	4.9	1.0	5.7	8.1	5.2	6.6	4.7	10.5	1.7	10.9
2,4-Dinitrophenol	60.4	16.3	68.9[b]	6.1	56.7	10.4	46.8	13.1	20.8	70.9
2,4-Dinitrotoluene	57.5	3.9	60.4	5.4	52.7	5.6	49.8	3.3	27.7	10.8
Hexachlorobenzene	0.1	42.5	0.2	12.0	0.1	43.3	0.1	0.0	0.0	
γ-BHC	3.4[b]	9.4	3.1	16.3	3.6	17.7	2.8[b]	12.1	5.0	22.3
β-BHC	5.3	8.5	5.4	13.3	5.5	2.9	4.8	2.4	4.0	18.2
METALS										
Lead	3.2[b]	3.6	1.4	4.3	1.3	31.4	1.5	16.1	6.3[b]	0.0
Cadmium	55.7	1.5	38.7	2.3	33.5	18.8	30.3	16.8	37.4	7.5
SURROGATES (In Leachate)										
2-Fluorophenol	62.0	5.3	65.8	6.5	58.2	2.5	59.3	4.1		
d_5-Phenol	77.0	6.2	83.3	5.4	71.7	1.5	70.1	2.9		
d_5-Nitrobenzene	64.5	3.2	71.8	8.3	65.5	4.4	62.5	1.5		
2-Fluorobiphenyl	62.0	3.7	70.1	8.4	59.1	4.0	60.5	6.9		
2,4,5-Tribromophenol	68.8	7.6	71.6	5.1	58.1	6.6	56.4	3.2		
d_{14}-p-Terphenyl	89.3	8.6	97.9	6.7	80.5	2.8	77.1	6.8		

[a] Triplicate Analyses.

[b] Duplicate Analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.[15]

RSDs for replicate leachings were usually less than 30 percent. The Method 1312 precision results for the eastern soil are much better than those of the previous TCLP study.

The recovery of lead from both the eastern and the western soils was very low and the precision was poor. The large RSDs are, in part, the result of the fact that analytical measurements were made near the quantitation limit of Method 6020 (ICP/MS). Cadmium had reasonable recovery (30 to 56 percent) from the eastern soil and its replicate leaching had recovery RSDs less than 20 percent. Cadmium recovery was only 4 to 9 percent from the western soil. The precision (variability) of the triplicate leachings of cadmium was much greater for the western soil (63 percent RSD versus 2.3 percent RSD at pH 4.0). Thus, cadmium showed a greater sensitivity to soil type in these experiments than did lead.

Both cadmium and lead recoveries are sensitive to the pH of the leaching fluid. Lead recovery, as shown in Table 1, is significantly greater when the pH 3.0 leaching fluid is used, although all of the lead recovery values are low (1.3 to 3.2 percent). Cadmium recovery is also greater when low pH leaching

TABLE 2. METHOD 1312 PRECISION RESULTS FROM WESTERN SOIL

FORTIFIED ANALYTES	Amount Spiked (µg)	pH = 4.2 High Spiking Level Avg. % Rec.[a]	pH = 4.2 High Spiking Level % RSD	pH = 5.0 Low Spiking Level[c] Avg. % Rec.[a]	pH = 5.0 Low Spiking Level[c] % RSD
bis(2-chloroethyl)-ether	1040	45.1	13.7	59.2	14.2
2-Chlorophenol	1620	58.9	28.6	32.4	54.9
1,4-Dichlorobenzene	2000	12.8	11.8	13.6	34.6
1,2-Dichlorobenzene	8920	15.0	6.0	17.0	28.4
2-Methylphenol	3940	40.5	12.2	28.6	32.6
Nitrobenzene	1010	36.1	14.6	45.2	21.3
2,4-Dimethylphenol	1460	3.6	23.3	1.2	87.6
Hexachlorobutadiene	6300	2.5	17.0	4.5	22.8
Acenaphthene	3640	22.2	20.6	8.4[b]	7.7
2,4-Dinitrophenol	1300	20.5	-	1.8[b]	15.7
2,4-Dinitrotoluene	1900	61.6	30.1	30.8	54.4
Hexachlorobenzene	1840	0.2	41.8	0.8	173.2
γ-BHC	7440	21.2	23.8[b]	16.6	55.2
β-BHC	640	13.2	33.7	10.2	51.7
METALS					
Lead	5000	0.3	27.0	0.2	51.7
Cadmium	1000	4.4	63.0	9.1	71.3
SURROGATES (In Leachate)					
2-Fluorophenol	200	65.1	7.5	34.4	60.6
d_5-Phenol	200	93.5	10.4	51.7	62.7
d_5-Nitrobenzene	100	41.4	52.4	46.4	10.6
2-Fluorobiphenyl	100	44.0	42.1	36.8	15.6
2,4,5-Tribromophenol	200	68.0	10.3	50.7	57.1
d_{14}-p-Terphenyl	100	100.1	8.1	87.7	13.6

[a] Triplicate Analyses.

[b] Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.[15]

[c] The low spiking level was 0.20 times the high spiking level.

fluid is used, but it varies over a greater range than lead (30 to 56 percent). The method precision for both metals is worst when the recoveries are lowest. Interestingly, lead recovery was low and only moderately higher when Method 1311 was used to leach the fortified eastern soil; this is in contrast to the results obtained in a recent interlaboratory study[12] that showed dramatically higher lead recoveries with Method 1311. The reason for this difference is not known but points out the need for further study on the sensitivity of leaching methods to soil type as well as to the metal species presented in the sample.

In contrast to results for the metals, the pH of the leaching fluid has little effect on either the recovery or the precision (variability) of replicate leachings for semi-volatile organic compounds. Periodic monitoring of the pH of the fluid during the leaching showed that the pH of the fluid changed negligibly after the first hour of the 18 hour leaching period. The final leachate pH for all the eastern soil samples was nearly the same (pH 4.57 to pH 4.64) for the pH 4, 5 and 6 fluids and was thus unaffected by the initial pH of the leaching fluid. The final leachate pH was low (pH 4.14) when pH 3.2 fluid was used. This might be partly responsible for the higher recovery observed for the metals with low pH leaching fluid.[13]

VOLATILE COMPOUNDS PRECISION

The precision of Method 1312 was evaluated by measuring the repeatability of recovery of 27 volatile organic compounds using four different types of soil. A summary of the precision data for these compounds is presented in Table 3. The recovery levels for individual replicate leachings used to calculate the average recoveries and %RSDs presented in Table 3 are given in Appendix A. Soil 1 was collected at a Superfund site west of the Mississippi River and Soil 2 came from a Superfund site in the eastern United States. Excluding isobutanol, a polar water soluble compound with known purging difficulties, the average recoveries for the target analytes ranged from 10 percent to 85 percent for Soil 1 and ranged from 7 percent to 89 percent for Soil 2. Twenty-two of the 26 (85 percent) analytes for Soil 1 and 17 of 26 (65 percent) analytes for Soil 2 had RSDs less than 20 percent. Only four analytes had RSDs greater than 50 percent; these analytes present significant analytical difficulties during the purge-and-trap GC/MS analysis (Method 8260). Vinyl chloride and the Freons are extremely volatile and are not trapped efficiently; acrylonitrile is water soluble and does not purge well. In general, recoveries were lower and RSDs were higher for the eastern soil than for the western soil. This matrix sensitivity appears most pronounced for carbon tetrachloride, ethylbenzene, tetrachloroethene, Freon 13 (trichlorofluoromethane) and Freon 113 (1,1,2-trichlorotrifluoroethane).

In general, replicate leachings of the sludge-contaminated soils (Soils 3 and 4 in Table 3) exhibited greater variability (larger RSD) than those of the Superfund soils (Soils 1 and 2). For Soil 3, 20 of the 27 volatile analytes had RSD values between 28 percent and 42 percent and 5 of the target analytes had RSDs greater than 50 percent. Ethyl acetate had highly variable recoveries ranging from 0 to 50 percent (Table 13, Appendix A), its lack of precision probably reflects the known difficulties associated with purging polar compounds from water. The sludge sample used to prepare Soil 3 contained acetone (120 ppm) which resulted in an apparent high recovery

TABLE 3. METHOD 1312 PRECISION RESULTS ON VOLATILE COMPOUNDS

Compound Name	Soil No. 1 Avg. % Rec.*	Soil No. 1 %RSD	Soil No. 2 Avg. % Rec.*	Soil No. 2 %RSD	Soil No. 3 Avg. % Rec.**	Soil No. 3 %RSD	Soil No. 4 Avg. % Rec.***	Soil No. 4 %RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethene	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl-1-propanol)	0.0	NA	0.0	NA	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.1	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

(116 percent) for acetone. For Soil 4, 19 of 27 volatile analytes had RSDs between 24 and 41 percent and only two compounds, both polar, ethyl acetate and acetone, had RSD values greater than 50 percent.

Three volatile surrogate compounds were spiked into the leachates of Soils 1-4 just prior to analysis by Method 8260. Surrogate recoveries (Appendix A, Tables 11 and 15) were consistently high (greater than 90 percent with RSDs less than 6 percent) and indicated that the purge-and-trap and GC/MS systems used in the volatile analyses were performing satisfactorily. The Method 1312 precision data reported for Soils 1 and 2 is in general agreement with that reported in a previous precision evaluation of the TCLP (Method 1311).[4] The RSDs reported in the TCLP study generally ranged from 3 percent to 20 percent for three different types of waste; volatile compound recoveries were found to be matrix and compound dependent.

RUGGEDNESS

The minor procedural variations used in the AOAC type ruggedness evaluation of Method 1312 for semi-volatile compounds and metals are listed in Table 4. Two levels of each experimental condition are assigned capital and lower case letters and are varied in the manner shown in the matrix given in Table 4. Table 5 presents the recovery data of each extractable from the eight ruggedness measurements. The group differences calculated from the recovery results of Table 5 are shown in Table 6. In columns V_a, V_c, and V_d, nearly all group difference values have the same sign; generally this indicates possible significance of the column variable. Usually any difference which is more than twice the standard deviation of the analytical methods is significant and should be further studied.[11,14] Most values in Column V_a are negative, which implies that the extractable compounds had greater recovery with pH 5.0 leaching fluid than with pH 4.2 fluid. However, since all the differences in Column V_a of Table 6 are less than twice the analyte standard deviations calculated from the RSDs and recoveries given for the western soil in Table 2, the V_a group differences are insignificant and careful control of leaching fluid pH does not appear to be a critical parameter for Method 1312. A similar comparison of analyte method precision with the mostly small differences given in Columns V_c and V_d leads to the same conclusion for the experimental parameters, particle size reduction and extractor vessel type. The other four variables, extraction time, liquid-solid ratio, extraction temperature, and number of filters used, do not appear to affect the performance of Method 1312. Since none of the seven variables tested is a critical parameter, Method 1312 appears rugged for the leaching of semi-volatile compounds and metals. These results concur with a previous ruggedness evaluation that demonstrated the TCLP to be "fairly rugged" for the semi-volatile organic analytes which were unaffected by variables B, D, and E in Table 4 in addition to the parameters: (a) headspace amount, (b) medium acidity, (c) acid washing of filter, and (d) filter type.[6,13] It is interesting to note that the EPA had previously intended to investigate extraction temperature but was unable to do so due to a lack of the laboratory equipment necessary to vary the temperature.[6] This study addressed this issue and determined that extraction temperature is not a critical method parameter for the leaching of semi-volatile organic compounds and metals.

The variables chosen for evaluation in the ruggedness test of Method 1312 for volatile organics are listed in Tables 7 and 8. Variables C and G are not method parameters, per se, they were chosen to determine the effect of analyte concentration upon compound recovery and to determine the effect of buffering the leaching fluid. Table 9 presents the compound recovery data resulting from the eight ruggedness measurements. The group differences calculated from the recovery results of Table 9 are given in Table 10. Since the differences in columns V_a, V_d, and V_e are generally small (absolute value less than 5) and of random sign, the variables leaching fluid pH, leaching fluid liquid/solid ratio, and extraction time, do not exhibit an observable effect on analyte recoveries and, thus, are not critical parameters for Method 1312. Due to the large magnitude of many values and the general uniformity of value sign, the variables associated with Columns V_b, V_c, and V_g may be significant. Particle size reduction (Column V_f) generally resulted in increased recoveries for the more highly volatile compounds. Smaller soil particle size probably decreases

TABLE 4. VARIABLES SELECTED FOR METHOD 1312 RUGGEDNESS TEST ON SEMI-VOLATILE COMPOUNDS

Parameter	Type	Rug 1	Rug 2	Rug 3	Rug 4	Rug 5	Rug 6	Rug 7	Rug 8
pH	A, a	A	A	A	A	a	a	a	a
Extraction time	B, b	B	B	b	b	B	B	b	b
Particle size	C, c	C	c	C	c	C	c	C	c
Extractor	D, d	D	D	d	d	d	d	D	D
Liquid/Solid Ratio	E, e	E	e	E	e	e	E	e	E
Temperature	F, f	F	f	f	F	F	f	f	F
Filter	G, g	G	g	g	G	g	G	G	g

A = 4.2 pH
a = 5.0 pH

B = 18 hr.
b = 16 hr.

C = not reduced
c = reduced (grinded)

D = standard vessel
d = bottle

E = ratio = 20 (2000 mL H_2O/100g)
e = ratio = 16 (1600 mL H_2O/100g)

F = Ambient approx. 77°F (25° C)
f = 60 - 65°F (16-18° C)

G = one filter
g = two filters

compound volatility loss during the soil spiking step by facilitating adsorption of the fortified compounds by increasing the surface area of the soil particles. As grinding a soil sample would increase the loss of environmentally incorporated analytes, particle size reduction should not be considered a critical method parameter in the leaching of real soil samples. Addition of 0.1M acetate buffer (Column V_g) adversely affected recoveries of virtually all the volatile compounds studied. This effect is probably the result, in large part, of chromatographic analysis difficulties caused by the loading of acetic acid onto the capillary GC column and/or into the purge and trap system used in Method 8260.[8] Fortifying the soil at lower concentration (i.e., 1 ppm versus 4 ppm) yielded better overall recoveries (Column V_c) for the more highly volatile compounds. This higher recovery may be related to limited analyte solubility in the purge vessel and/or could result from less compound loss during the soil spiking step. Interestingly, the only

TABLE 5. RUGGEDNESS EVALUATION OF METHOD 1312 ON FORTIFIED WESTERN SOIL

	Amount Spiked (μg)	Percent Recovery							
		Rug.1	Rug.2	Rug.3	Rug.4	Rug.5	Rug.6	Rug.7	Rug.8
FORTIFIED ANALYTES									
bis(2-Chloroethyl)-ether	1040.0	95.0	96.2	85.5	89.4	93.2	45.3	93.4	99.7
2-Chlorophenol	1620.0	55.3	70.9	61.5	73.8	69.6	39.0	80.8	76.8
1,4-Dichlorobenzene	2000.0	25.1	30.7	22.3	20.2	26.2	12.5	27.6	29.7
1,2-Dichlorobenzene	8920.0	25.9	35.3	25.6	22.2	30.7	29.7	30.2	36.0
2-Methylphenol	3940.0	66.4	71.7	63.5	69.9	66.0	75.7	68.2	78.4
Nitrobenzene	1010.0	79.5	81.1	72.0	74.4	76.8	39.4	76.1	82.2
2,4-Dimethylphenol	1460.0	10.4	12.2	7.6	12.6	8.0	5.4	7.7	12.4
Hexachlorobutadiene	6300.0	3.0		0.8	1.4	4.2	0.6	3.1	5.6
Acenaphthene	3640.0	31.1	32.0	18.5	25.9	32.1	12.1	29.1	36.8
2,4-Dinitrophenol	1300.0	7.9	49.7	3.3	54.8	41.3	49.2	58.5	56.1
2,4-Dinitrotoluene	1900.0	75.8	77.2	74.5	74.4	81.7	38.9	74.2	87.8
Hexachlorobenzene	1840.0	0.5	0.2	0.3	0.4	0.5	0.2	0.3	0.3
γ-BHC	7440.0	18.0	12.5	14.2	14.7	17.5	8.5	17.1	26.5
β-BHC	640.0	20.1		26.8	17.2	18.1	8.7	16.0	21.1
METALS									
Lead	5000.0	0.2	0.3	0.7	0.8	0.5	0.2	0.2	0.3
Cadmium	1000.0	0.9	7.3	9.7	2.9	15.8	2.3	12.8	4.2
SURROGATES (In Leachate)									
2-Fluorophenol	200.0	30.0	54.5	43.8	62.2	56.7	32.1	62.8	64.5
d_5-Phenol	200.0	86.0	86.6	89.3	98.4	90.3	49.7	98.7	90.4
d_5-Nitrobenzene	100.0	69.8	53.2	63.4	66.3	69.3	34.2	67.3	72.7
2-Fluorobiphenyl	100.0	61.1	65.7	59.2	60.0	61.8	29.8	67.0	61.5
2,4,6-Tribromophenol	200.0	48.1	64.0	35.6	68.1	59.9	33.6	62.3	74.5
d_{14}-p-Terphenyl	100.0	104.9	90.8	96.8	96.4	104.0	51.4	99.3	107.1

experimental parameter of importance appears to be the type of ZHE used. The Millipore ZHE gave higher recovery than the Associated Design ZHE for nearly all the organic compounds. This result is surprising given our experience with leakage difficulties associated with use of the Millipore ZHE and is in contrast with the results of a previous ruggedness evaluation of the TCLP for volatile compounds.[7] In that study, the only critical parameter identified was the type of ZHE; the Millipore ZHE produced lower analyte recoveries than the Associated Design ZHE and had notable leakage problems. The reason for this major discrepancy is not known but it may be related to operator experience with the different ZHE devices in the different laboratories.

TABLE 6. RUGGEDNESS TEST RESULTS - GROUP DIFFERENCES FOR SEMI-VOLATILE TEST COMPOUNDS

FORTIFIED ANALYTES	Va	Vb	Vc	Vd	Ve	Vf	Vg
bis(2-Chloroethyl)-ether	-2.70	1.75	-2.20	6.40	-0.35	2.90	-1.55
2-Chlorophenol	-10.92	-4.77	-8.08	0.23	-5.88	-3.93	2.27
1,4-Dichlorobenzene	-2.52	1.77	-1.07	4.88	-0.67	-1.08	-2.77
1,2-Dichlorobenzene	-4.40	1.90	-2.70	4.80	-0.30	-1.50	-4.90
2-Methylphenol	-4.20	-0.05	-7.90	2.40	2.05	0.40	0.15
Nitrobenzene	-1.72	2.87	-3.03	4.22	1.03	1.23	-0.82
2,4-Dimethylphenol	1.00	0.25	-3.55	0.95	0.15	1.30	0.30
Hexachlorobutadiene	-2.25	-0.60	0.70	1.00	0.50	2.25	-0.45
Acenaphthene	-3.70	2.30	-2.05	7.05	-2.10	5.50	-2.25
2,4-Dinitrophenol	-22.35	-6.15	-24.70	5.90	-21.95	-0.15	5.00
2,4-Dinitrotoluene	-4.90	0.40	-2.75	1.65	2.10	4.00	-4.75
Hexachlorobenzene	0.00	0.05	0.10	-0.05	-0.00	0.15	0.05
γ-BHC	-4.68	-1.88	-0.97	2.68	3.47	3.97	-0.97
β-BHC	-2.15	-6.35	6.30	-5.60	8.55	4.05	1.20
Lead	0.20	-0.20	0.0	-0.55	-0.10	0.10	-0.10
Cadmium	-3.6	-0.80	7.7	-1.85	-5.42	-2.08	-3.30

TABLE 7. VARIABLES SELECTED FOR METHOD 1312 RUGGEDNESS TESTING FOR VOLATILE COMPOUNDS

Variable	Upper case(A)	Lower case(a)	Experiment Number 1	2	3	4	5	6	7	8
Leaching fluid pH	4.1	4.3	A	A	A	A	a	a	a	a
ZHE apparatus	MP	AD	B	B	b	b	B	B	b	b
Analyte soil conc.*	0.8 ppm	4 ppm	C	c	C	c	C	c	C	c
Extraction time	20 hrs	16 hrs	D	D	d	d	d	d	D	D
Liquid/solid ratio	22:1	18:1	E	e	E	e	e	E	e	E
Particle size reduction	with	without	F	f	f	F	F	f	f	F
Buffer addition	with	without	G	g	g	G	g	G	G	g
% Recovery of analytes			s	t	u	v	w	x	y	z

*Fortified soil nominal concentration level. Refer to Table 8 below for experiment dependent fortification levels.

Abbreviations

MP: Millipore
AD: Associated Design
ppm: mg/kg

TABLE 8. SOIL FORTIFICATION LEVELS FOR RUGGEDNESS EXPERIMENTS

Variable Combination	Solid/Liquid Ratio	Sample grams	Leachate mL	Spike Level mg/kg	Max. Leachate Conc. µg/kg
C E	1:22	22	484	0.88	40
c E	1:22	22	484	4.40	200
C e	1:18	22	396	0.72	40
c e	1:18	22	396	3.60	200

TABLE 9. RUGGEDNESS TEST RESULTS FOR METHOD 1312 PERCENT RECOVERIES FOR VOLATILE TEST COMPOUNDS

Compound Name	Experiment Number							
	1	2	3	4	5	6	7	8
Chloromethane	49	39	42	36	73	27	26	44
Bromoethane	60	39	52	46	64	30	34	40
Vinyl chloride	37	26	27	25	59	21	16	32
Chloroethane	60	59	65	47	115	35	38	59
Methylene chloride	134	76	126	63	179	47	67	78
Acetone	312	40	73	96	199	60	87	74
Carbon disulfide	60	43	48	43	71	31	38	48
1,1-Dichloroethene	47	34	33	38	62	23	24	44
1,1-Dichloroethane	73	60	64	58	81	40	49	59
trans-1,2-Dichloroethene	63	49	51	48	73	36	42	52
Chloroform	82	33	47	128	65	45	113	29
1,2-Dichloroethane	71	61	67	56	67	55	52	57
2-Butanone	78	42	53	66	35	51	63	42
1,1,1-Trichloroethane	55	41	44	47	61	35	38	49
Carbon tetrachloride	52	38	41	44	58	34	36	48
Bromodichloromethane	80	63	68	66	68	55	61	62
1,1,2,2-Tetrachloroethane	67	61	69	54	63	62	54	58
1,2-Dichloropropane	70	71	66	60	71	51	53	60
cis-1,3-Dichloropropene	92	76	82	71	76	71	67	75
Trichloroethene	56	47	49	50	56	44	43	51
Dibromochloromethane	70	56	64	60	62	60	57	59
1,1,2-Trichloroethane	74	59	69	58	68	59	85	64
Benzene	69	52	57	52	63	49	51	52
trans-1,3-Dichloropropene	74	63	66	58	64	55	49	61
Bromoform	60	55	62	55	58	61	52	57
4-Methyl-2-pentanone	147	49	44	117	39	136	114	48
Tetrachloroethene	44	38	39	35	40	36	33	40
Toluene	68	53	61	52	63	49	48	54
Chlorobenzene	61	51	59	48	54	50	51	51
Ethylbenzene	57	49	52	42	51	40	43	49
Styrene	44	46	51	36	44	42	39	44
p-Xylene	52	49	49	42	47	42	41	46
o-Xylene	58	49	57	43	55	48	47	49
1,4-Dichlorobenzene	33	32	34	25	27	32	28	30
Trichlorofluoromethane	36	24	20	60	55	14	26	37
Acrylonitrile	81	67	74	46	61	65	11	63
n-Butanol	0	0	0	0	0	0	0	0
Ethyl acetate	43	10	50	36	0	56	0	0
Ethyl ether	68	58	58	62	58	58	0	58
Isobutanol	0	0	0	0	0	0	0	0
1,1,2-Trichlorotrifluoroethane (Freon 113)	28	19	15	26	49	11	11	28
1,1,1,2-Tetrachloroethane	66	57	64	56	65	57	52	58

NOTE: n-Butanol and isobutanol were not recovered in any of the ruggedness experiments.

TABLE 10. RUGGEDNESS TEST RESULTS FOR METHOD 1312 GROUP DIFFERENCES FOR VOLATILE TEST COMPOUNDS

Compound Name	Conditions						
	Va	Vb	Vc	Vd	Ve	Vf	Vg
Chloromethane	-6	13	16	0	0	12	-18
Bromoethane	1	11	20	2	6	8	-12
Vinyl chloride	-9	11	14	0	-3	11	-11
Chloroethane	-7	24	23	-8	-1	18	-38
Methylene chloride	-2	34	69	-7	8	26	-45
Acetone	7	76	119	40	30	87	37
Carbon disulfide	-5	12	19	5	3	10	-15
1,1-Dichloroethene	-6	11	13	4	1	13	-14
1,1-Dichloroethane	0	15	19	6	6	8	-20
trans-1,2-Dichloroethene	-5	13	18	7	4	8	-15
Chloroform	-1	17	29	4	6	6	9
1,2-Dichloroethane	5	3	8	0	1	3	-2
2-Butanone	8	-3	11	9	6	-1	20
1,1,1-Trichloroethane	1	5	7	-1	0	14	-6
Carbon tetrachloride	-1	4	6	-1	1	13	-6
Bromodichloromethane	7	3	9	3	3	6	-1
1,1,2,2-Tetrachloroethane	3	3	5	-2	4	-1	-2
1,2-Dichloropropane	8	7	5	2	-1	5	-10
cis-1,3-Dichloropropene	8	3	6	3	5	5	1
Trichloroethene	1	3	4	1	2	6	-3
Dibromochloromethane	1	2	7	1	4	2	2
1,1,2-Trichloroethane	3	1	7	0	4	5	-1
Benzene	3	6	9	1	3	6	-1
trans-1,3-Dichloropropene	8	4	4	1	4	6	-3
Bromoform	-1	2	3	-2	5	-2	-1
4-Methyl-2-pentanone	31	38	-27	-20	40	28	58
Tetrachloroethene	1	2	2	2	2	3	-1
Toluene	4	4	9	1	3	5	-3
Chlorobenzene	2	1	7	2	4	0	-1
Ethylbenzene	4	3	6	4	3	4	-5
Styrene	-1	-1	6	3	2	-6	-4
p-Xylene	1	2	5	5	1	-1	-2
o-Xylene	0	2	9	2	3	-1	-2
1,4-Dichlorobenzene	-1	-1	4	4	1	-6	2
Trichlorofluoromethane	-7	10	9	2	-1	17	-13
Acrylonitrile	10	13	4	2	17	1	-8
n-Butanol	0	0	0	0	0	0	0
Ethyl acetate	11	-5	8	-12	16	-20	29
Ethyl ether	7	5	-2	-2	5	7	0
Isobutanol	0	0	0	0	0	0	0
1,1,2-Trichlorotrifluoroethane (Freon-113)	-7	10	9	1	-3	15	-12
1,1,1,2-Tetrachloroethane	2	4	6	-1	4	3	-4

NOTE: n-Butanol and isobutanol were not recovered in any of the ruggedness experiments.

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APPENDIX A

PERFORMANCE TESTING OF METHOD 1312

PART 1. SEMI-VOLATILE COMPOUNDS AND METALS

1.1 EXPERIMENTAL DESIGN

Two different types of soil were used for the organic semi-volatile and inorganic (metals) precision and ruggedness evaluations of Method 1312: soil with high organic content (clay) from the east coast, and soil with low organic content (sandy type) from the west coast. Both soils were prescreened to make sure that no appreciable amount of hazardous organic compounds or metals were present (especially those compounds that would be fortified for the validation study) that might interfere with sample analysis and/or data interpretation.

Analytes selected to be fortified into the soils, as well as their spiking levels, are listed in Tables A-1 through A-7. These compounds were chosen to include analytes with different volatilities and polarities and with a wide range of acidic and basic properties based on our previous experience with Methods 1310 and 1311.

In addition to measuring method precision, the effect of extraction fluid pH was also investigated. The eastern soil was leached according to the Method 1312 procedure by using four different pH values ranging from pH = 3 to pH = 6 in triplicates. The pH of the leaching fluid was also monitored during the 18-hour extraction period and the recoveries of each analyte were determined by GC/MS and ICP/MS. Similarly, the western soil was analyzed 6 times, each at pH = 4.2 and at pH = 5 for additional precision data.

1.2 EXPERIMENTAL PROCEDURE

A cocktail spiking solution containing various amounts of all the semi-volatile spiking compounds was prepared and an appropriate amount of this solution was used to spike 100 g of soil sample. The soil and the spiking solution were mixed and left at 4° C for overnight. The sample was then wetted by adding 50 mL of water in which appropriate amounts of metals (lead and cadmium) were also present. This mixture was allowed to sit at 4° C for overnight prior to the extraction procedure. For the extraction and the analysis of the leachate, refer to Method 1312 (Appendix C).

TABLE A-1. PRECISION RESULTS FROM EASTERN SOIL - EXTRACTION FLUID pH = 3.2

	Amount Spiked (μg)	Amount Found (μg)			Avg. % Rec.	Avg. Found (μg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-chloroethyl)-ether	920.0	639.9	678.7	768.3	75.6	695.6	65.9	9.5
2-Chlorophenol	2360.0	1377.7	1371.2	1595.8	61.4	1448.2	127.8	8.8
1,4-Dichlorobenzene	1960.0	302.0	299.6	329.1	15.8	310.3	16.4	5.3
1,2-Dichlorobenzene	16160.0	1524.4	1776.3	2260.1	11.5	1853.6	373.9	20.2
2-Methylphenol	4440.0	1923.9	2078.8	2337.6	47.6	2113.4	209.0	9.9
Nitrobenzene	1120.0	814.4	798.1	835.6	72.9	816.0	18.8	2.3
2,4-Dimethylphenol	2720.0	324.9	368.1	309.8	12.3	334.2	30.3	9.1
Hexachlorobutadiene	17520.0	219.1	205.0	216.4	1.2	213.5	7.5	3.5
Acenaphthene	3120.0	151.0	154.1	152.6	4.9	152.6	1.5	1.0
2,4-Dinitrophenol	1240.0	856.0	773.8	615.9	60.4	748.6	122.0	16.3
2,4-Dinitrotoluene	1920.0	1076.1	1084.2	1153.5	57.5	1104.6	42.6	3.9
Hexachlorobenzene	2380.0	4.1	3.9	1.6	0.1	3.2	1.4	42.5
γ-BHC	16120.0	591.8	517.9	a	3.4	554.8	52.3	9.4
β-BHC	640.0	34.6	36.7	31.0	5.3	34.1	2.9	8.5
METALS								
Lead	5000.0	a	156.9	165.1	3.2	161.0	5.8	3.6
Cadmium	1000.0	550.3	566.6	554.3	55.7	557.1	8.5	1.5
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	131.7	120.0	120.4	62.0	124.0	6.6	5.3
d_5-Phenol	200.0	165.1	148.8	148.2	77.0	154.0	9.6	6.2
d_5-Nitrobenzene	100.0	66.0	65.4	62.2	64.5	64.5	2.1	3.2
2-Fluorobiphenyl	100.0	64.0	62.6	59.5	62.0	62.0	2.3	3.7
2,4,6-Tribromophenol	200.0	145.5	141.4	125.7	68.8	137.6	10.4	7.6
d_{14}-p-Terphenyl	100.0	93.7	93.7	80.5	89.3	89.3	7.6	8.6

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

TABLE A-2. PRECISION RESULTS FROM EASTERN SOIL - EXTRACTION FLUID pH = 4.0

	Amount Spiked (µg)	Amount Found (µg)			Avg. % Rec.	Avg. Found (µg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	920.0	685.1	844.6	684.1	80.2	737.9	92.4	12.5
2-Chlorophenol	2360.0	1382.4	1580.8	1464.2	62.5	1475.8	99.7	6.8
1,4-Dichlorobenzene	1960.0	301.4	382.4	327.2	17.2	337.0	41.4	12.3
1,2-Dichlorobenzene	16160.0	1717.8	1995.9	1777.5	11.3	1830.4	146.4	8.0
2-Methylphenol	4440.0	1930.5	2249.5	2126.0	47.3	2102.0	160.9	7.7
Nitrobenzene	1120.0	826.2	1000.0	875.3	80.4	900.5	89.6	10.0
2,4-Dimethylphenol	2720.0	321.1	449.9	345.6	13.7	372.2	68.4	18.4
Hexachlorobutadiene	17520.0	225.0	290.8	251.9	1.5	255.9	33.1	12.9
Acenaphthene	3120.0	169.9	193.7	167.7	5.7	177.1	14.4	8.1
2,4-Dinitrophenol	1240.0	a	818.0	891.6	68.9	854.8	52.0	6.1
2,4-Dinitrotoluene	1920.0	1116.6	1231.1	1128.8	60.4	1158.8	62.9	5.4
Hexachlorobenzene	2380.0	4.3	5.1	4.1	0.2	4.5	0.5	12.0
γ-BHC	16120.0	571.8	529.7	413.1	3.1	504.8	82.2	16.3
β-BHC	640.0	30.3	39.3	33.5	5.4	34.4	4.6	13.3
METALS								
Lead	5000.0	71.6	69.5	75.7	1.4	72.3	3.1	4.3
Cadmium	1000.0	392.6	376.3	390.6	38.7	386.5	8.9	2.3
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	123.5	130.9	140.7	65.8	131.7	8.6	6.5
d_5-Phenol	200.0	156.2	170.1	173.2	83.3	166.5	9.0	5.4
d_5-Nitrobenzene	100.0	65.2	76.9	73.2	71.8	71.8	6.0	8.3
2-Fluorobiphenol	100.0	63.4	72.6	74.4	70.1	70.1	5.9	8.4
2,4,6-Tribromophenol	200.0	135.0	145.6	148.9	71.6	143.2	7.3	5.1
d_{14}-p-Terphenyl	100.0	92.4	105.1	96.1	97.9	97.9	6.5	6.7

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

TABLE A-3. PRECISION RESULTS FROM EASTERN SOIL - EXTRACTION FLUID pH = 5.0

	Amount Spiked (μg)	Amount Found (μg)			Avg. % Rec.	Avg. Found (μg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	920.0	676.6	633.7	604.6	69.4	638.3	36.2	5.7
2-Chlorophenol	2360.0	1323.8	1105.9	1259.2	52.1	1229.6	111.9	9.1
1,4-Dichlorobenzene	1960.0	340.8	322.9	279.3	16.0	314.3	31.7	10.1
1,2-Dichlorobenzene	16160.0	1816.2	1432.8	1574.0	9.9	1607.7	193.9	12.1
2-Methylphenol	4440.0	1905.0	1642.7	1832.3	40.4	1793.3	135.5	7.6
Nitrobenzene	1120.0	783.0	746.7	718.4	66.9	749.4	32.4	4.3
2,4-Dimethylphenol	2720.0	a	230.1	228.8	8.4	229.4	0.9	0.4
Hexachlorobutadiene	17520.0	225.6	226.0	203.8	1.2	218.5	12.7	5.8
Acenaphthene	3120.0	174.6	161.4	153.4	5.2	163.1	10.7	6.6
2,4-Dinitrophenol	1240.0	668.4	653.8	787.0	56.7	703.1	73.1	10.4
2,4-Dinitrotoluene	1920.0	1056.6	948.5	1030.8	52.7	1012.0	56.5	5.6
Hexachlorobenzene	2380.0	2.0	4.0	2.0	0.1	2.7	1.2	43.3
γ-BHC	16120.0	665.9	621.5	468.8	3.6	585.4	103.4	17.7
β-BHC	640.0	34.3	36.3	34.9	5.5	35.2	1.0	2.9
METALS								
Lead	5000.0	60.5	88.8	48.4	1.3	65.9	20.7	31.4
Cadmium	1000.0	276.5	326.9	401.6	33.5	335.0	62.9	18.8
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	118.3	113.0	117.6	58.2	116.3	2.9	2.5
d^5-Phenol	200.0	143.7	141.3	145.5	71.7	143.5	2.1	1.5
d_5-Nitrobenzene	100.0	65.0	68.6	63.0	65.5	65.5	2.9	4.4
2-Fluorobiphenol	100.0	61.1	56.5	59.7	59.1	59.1	2.4	4.0
2,4,6-Tribromophenol	200.0	115.2	109.0	124.3	58.1	116.2	7.7	6.6
d_{14}-p-Terphenyl	100.0	82.9	78.7	79.7	80.5	80.5	2.2	2.8

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

TABLE A-4. EASTERN SOIL RECOVERY BY METHOD 1312 - EXTRACTION FLUID pH = 6.1

	Amount Spiked (µg)	Amount Found (µg)			Avg. % Rec.	Avg. Found (µg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	920.0	628.8	634.0	699.2	71.1	654.0	39.2	6.0
2-Chlorophenol	2360.0	1299.0	1256.0	1497.6	57.2	1350.9	128.9	9.5
1,4-Dichlorobenzene	1960.0	262.4	302.2	336.4	15.3	300.3	37.0	12.3
1,2-Dichlorobenzene	16160.0	1474.4	1653.6	2208.0	11.0	1778.7	382.5	21.5
2-Methylphenol	4440.0	1768.8	1811.0	2208.0	43.5	1929.3	242.3	12.6
Nitrobenzene	1120.0	700.0	737.6	763.2	65.5	733.6	31.8	4.3
2,4-Dimethylphenol	2720.0	221.6	207.4	208.2	7.8	212.4	8.0	3.8
Hexachlorobutadiene	17520.0	179.2	217.6	234.4	1.2	210.4	28.3	13.4
Acenaphthene	3120.0	132.0	145.2	162.8	4.7	146.7	15.5	10.5
2,4-Dinitrophenol	1240.0	649.6	590.4	499.2	46.8	579.7	75.8	13.1
2,4-Dinitrotoluene	1920.0	920.0	976.6	971.2	49.8	955.9	31.2	3.3
Hexachlorobenzene	2380.0	2.0	2.0	2.0	0.1	2.0	0.0	0.0
γ-BHC	16120.0	408.0	484.6	a	2.8	446.3	54.3	12.1
β-BHC	640.0	30.4	30.6	31.8	4.8	30.9	0.8	2.4
METALS								
Lead	5000.0	76.0	62.0	86.0	1.5	74.7	12.1	16.1
Cadmium	1000.0	328.0	336.0	244.0	30.3	302.7	51.0	16.8
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	124.0	114.6	117.4	59.3	118.7	4.8	4.1
d_5-Phenol	200.0	142.8	135.4	142.2	70.1	140.1	4.1	2.9
d_5-Nitrobenzene	100.0	61.8	63.6	62.2	62.5	62.5	0.9	1.5
2-Fluorobiphenol	100.0	56.8	59.6	65.0	60.5	60.5	4.2	6.9
2,4,6-Tribromophenol	200.0	116.0	108.8	113.4	56.4	112.7	3.6	3.2
d_{14}-p-Terphenyl	100.0	78.8	81.2	71.2	77.1	77.1	5.2	6.8

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

TABLE A-5. PRECISION RESULTS (FOR COMPARISON) FROM EASTERN SOIL EXTRACTED BY METHOD 1311

	Amount Spiked (µg)	Amount Found (µg)			Avg. % Rec.	Avg. Found (µg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	920.0	452.4	507.2	603.2	56.6	520.9	76.3	14.7
2-Chlorophenol	2360.0	960.0	873.4	1176.0	42.5	1003.1	155.9	15.5
1,4-Dichlorobenzene	1960.0	142.4	175.2	145.6	7.9	154.4	18.1	11.7
1,2-Dichlorobenzene	16160.0	1328.0	1398.4	1245.6	8.2	1324.0	76.5	5.8
2-Methylphenol	4440.0	1720.0	1608.0	2104.0	40.8	1810.7	260.1	14.4
Nitrobenzene	1120.0	448.0	496.0	576.0	45.2	506.7	64.7	12.8
2,4-Dimethylphenol	2720.0	93.6	79.4	133.6	3.8	102.2	28.1	27.5
Hexachlorobutadiene	17520.0	52.8	52.8	34.6	0.3	46.7	10.5	22.4
Acenaphthene	3120.0	53.6	56.0	45.3	1.7	51.6	5.6	10.9
2,4-Dinitrophenol	1240.0	49.8	332.6	392.8	20.8	258.4	183.2	70.9
2,4-Dinitrotoluene	1920.0	469.6	542.4	583.2	27.7	531.7	57.5	10.8
Hexachlorobenzene	2380.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
γ-BHC	16120.0	769.0	646.4	1000.0	5.0	805.1	179.5	22.3
β-BHC	640.0	21.2	24.8	30.4	4.0	25.5	4.6	18.2
METALS								
Lead	5000.0	316.0	a	316.0	6.3	316.0	0.0	0.0
Cadmium	1000.0	348.0	370.0	404.0	37.4	374.0	28.2	7.5

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

1.3 ANALYTICAL INSTRUMENTATION

Analyses of the leachate for semi-volatile compounds were performed by using a Finnigan 4023 GC/MS. The GC was equipped with a DB-5 capillary column (or equivalent) 30 meters long, 1 micron film thickness, and 0.32 mm internal diameter. The temperature in the GC oven was programmed from 30° C to 300° C at 8° C per minute with an initial hold at 30° C for 4 minutes. For mass spectrometer quantitation, the procedures in the latest SW-846 version were followed, with all the QA/QC criteria specified in the SOW (Statement of Work) being achieved. Metals were analyzed by ICP/MS using the VG Model Plasmaquad-I following the analysis procedure of SW-846 draft Method 6020.

TABLE A-6. PRECISION RESULTS FROM WESTERN SOIL SPIKED AT HIGH LEVELS - EXTRACTION FLUID pH = 4.2 ± 0.1

	Amount Spiked (µg)	Amount Found (µg)			Avg. % Rec.	Avg. Found (µg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	1040.0	495.2	515.9	395.7	45.1	468.9	64.3	13.7
2-Chlorophenol	1620.0	1015.3	654.7	1190.2	58.9	953.4	273.1	28.6
1,4-Dichlorobenzene	2000.0	260.7	282.7	223.0	12.8	255.5	30.2	11.8
1,2-Dichlorobenzene	8920.0	1319.6	1428.6	1270.0	15.0	1339.4	81.1	6.1
2-Methylphenol	3940.0	1614.4	1392.6	1781.0	40.5	1596.0	194.9	12.2
Nitrobenzene	1010.0	404.7	385.2	304.5	36.1	364.8	53.1	14.6
2,4-Dimethylphenol	1460.0	63.0	57.6	39.3	3.7	53.3	12.4	23.3
Hexachlorobutadiene	6300.0	152.8	187.0	134.1	2.5	158.0	26.8	17.0
Acenaphthene	3640.0	919.0	616.5	888.1	22.2	807.9	166.4	20.6
2,4-Dinitrophenol	1300.0	266.0	N/A	N/A	20.5	266.0		
2,4-Dinitrotoluene	1900.0	1354.9	764.6	1393.0	61.6	1170.8	352.3	30.1
Hexachlorobenzene	1840.0	1.6	4.0	3.1	0.2	2.9	1.2	41.8
γ-BHC	7440.0	1842.0	1311.2	N/A	21.2	1576.6	375.3	23.8
β-BHC	640.0	107.1	52.5	93.8	13.2	84.5	28.5	33.7
METALS								
Lead	5000.0	12.9	15.6	21.7	0.3	16.7	4.5	27.0
Cadmium	1000.0	36.0	75.0	21.2	4.4	44.1	27.8	63.1
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	122.6	141.3	127.1	65.2	130.3	9.8	7.5
d_5-Phenol	200.0	176.9	209.6	174.7	93.5	187.1	19.5	10.4
d_5-Nitrobenzene	100.0	35.5	65.5	23.3	41.4	41.4	21.7	52.4
2-Fluorobiphenyl	100.0	38.7	64.6	28.7	44.0	44.0	18.5	42.1
2,4,6-Tribromophenol	200.0	146.8	120.2	141.0	68.0	136.0	14.0	10.3
d_{14}-p-Terphenyl	100.0	103.8	105.6	90.8	100.1	100.1	8.1	8.1

TABLE A-7. PRECISION RESULTS FROM WESTERN SOIL SPIKED AT LOW LEVELS - EXTRACTION FLUID pH = 5.0 ± 0.1

	Amount Spiked (μg)	Amount Found (μg)			Avg. % Rec.	Avg. Found (μg)	SD	%RSD
		Set 1	Set 2	Set 3				
FORTIFIED ANALYTES								
bis(2-Chloroethyl)-ether	208.0	112.2	114.0	143.3	59.2	123.2	17.5	14.2
2-Chlorophenol	324.0	171.0	77.9	65.7	32.4	104.9	57.6	54.9
1,4-Dichlorobenzene	400.0	38.1	50.4	75.2	13.6	54.6	18.9	34.6
1,2-Dichlorobenzene	1724.0	218.8	277.1	382.6	17.0	292.8	83.0	28.4
2-Methylphenol	788.0	310.3	188.8	177.6	28.6	225.6	73.6	32.6
Nitrobenzene	202.0	76.0	84.9	113.3	45.2	91.4	19.5	21.3
2,4-Dimethylphenol	292.0	0.0	4.6	5.5	1.2	3.4	3.0	87.6
Hexachlorobutadiene	1260.0	42.0	66.3	61.8	4.5	56.7	12.9	22.8
Acenaphthene	728.0	57.9	64.6	a	8.4	61.2	4.7	7.7
2,4-Dinitrophenol	260.0	a	4.8	4.1	1.8	4.6	0.3	15.7
2,4-Dinitrotoluene	380.0	111.2	56.7	183.7	30.8	117.2	63.7	54.4
Hexachlorobenzene	368.0	0.0	0.0	8.4	0.8	2.8	4.8	173.2
γ-BHC	1488.0	345.4	91.2	303.9	16.6	246.8	136.4	55.2
β-BHC	128.0	15.4	8.7	19.0	11.2	14.4	5.2	36.4
METALS								
Lead	5000.0	3.4	11.5	9.7	0.2	8.2	4.2	51.7
Cadmium	1000.0	28.0	158.2	87.9	9.1	91.4	65.2	71.3
SURROGATES (In Leachate)								
2-Fluorophenol	200.0	114.1	59.6	32.4	34.4	68.7	41.6	60.6
d_5-Phenol	200.0	174.2	89.6	46.6	51.7	103.5	64.9	62.7
d_5-Nitrobenzene	100.0	42.0	45.4	51.7	46.4	46.4	4.9	10.6
2-Fluorobiphenyl	100.0	32.4	34.7	43.3	36.8	36.8	5.7	15.6
2,4,6-Tribromophenol	200.0	154.1	110.5	39.4	50.7	101.3	57.9	57.1
d_{14}-p-Terphenyl	100.0	78.3	101.1	83.7	87.7	87.7	11.9	13.6

a: Value was rejected as an outlier using the Dixon Q-test at the 90% confidence level.[15]

PART 2 - VOLATILE ORGANIC COMPOUNDS

The volatile organic part of the Method 1312 Single Laboratory Precision and Ruggedness Study was performed by two separate laboratories (Acurex under subcontract with LESC and Midwest Research Institute under subcontract with Acurex). Midwest Research Institute (MRI) performed triplicate analyses on the two soils from contaminated Superfund sites for the precision study. The experimental procedures, results and discussions are presented in Section 2.1. Acurex performed additional precision studies by using soils contaminated with municipal sludges (California Model Urban Soils). Six replicate analyses were performed for precision evaluation.

2.1 SOILS FROM CONTAMINATED SUPERFUND SITES (EAST AND WEST)

2.1.1 Experimental Procedures

2.1.1.1 Sample Preparation and Leaching--

Samples used by MRI include contaminated soil from Superfund sites west of Mississippi River (Soil 1) and east of Mississippi River (Soil 2). The soils were treated as follows. The contents of the eight volatile organic analysis (VOA) vials containing the soils were combined and spread on a precleaned sheet of aluminum foil. The soils were then allowed to air dry overnight in a fume hood.

The ZHEs were assembled with the piston about 1/2 inch from the top of the cylinder. Twenty-five (25) grams of the pretreated soils were transferred and spread out evenly over the top of the piston and spiked with 12-32 µg/g of a spiking solution containing the target analytes. The top plate of the ZHE was immediately fitted onto the device and the samples were mixed for at least 1 hour by rotating end over end. At the end of this period, the ZHE was opened, the filter assembly put in place, and the device rapidly sealed. The appropriate leaching fluid (refer to Appendix C) was pumped into the ZHEs (500 mL of Fluid 1 for Soil 2, and 500 mL of Fluid 2 for Soil 1). After exclusion of the headspace in the device, the ZHEs were rotated as per Method 1312 for 16 hours.

At the end of the extraction period, a 50-mL gastight syringe was connected to the Luer lock port on the ZHE, and pressure was applied to the device. The first 10 mL collected was used to rinse the syringe and discarded. The syringe was then used to collect 45 to 50 mL of the leachate, which was slowly dispensed into precleaned VOA vials to overflowing. The vials were sealed and placed inverted into a can, which was sealed and placed in a refrigerator (4° C) until analysis.

The above procedure was performed in triplicate. After the spiked matrices were extracted, the same protocol was used for the unspiked matrix samples, and again for a device blank (no matrix, used to determine memory effects).

2.1.1.2 Leachate Analysis--

All of the leachates thus obtained (3 spiked matrices, 1 unspiked matrix, and 1 device blank) were analyzed by SW-846 Method 8260 (Appendix E) for the target analytes. In addition, the leachates for unspiked Soil 1 and Soil 2 were used for analysis of one matrix spike each (Tables A-8 through A-10).

TABLE A-8. RESULTS FOR SPIKED SOIL NO. 1 LEACHATES

	Amount Found (µg/L)				Amount Spiked (µg/L)		% Recovery (a)				
Analyte	Native Level	Spiked Set 1	Spiked Set 2	Spiked Set 3	Set 1	Set 2,3	Set 1	Set 2	Set 3	Avg (b)	%RSD (c)
Acetone	18.5	618	707	645	1,200	1,600	49.9	43.1	39.1	44.0	12.4
Acrylonitrile	ND	66.7	607	563	600	800	11.1	75.1	74.9	52.5	68.4
Benzene	1.18	315	362	369	600	800	52.4	45.1	46.0	47.8	8.29
n-Butyl alcohol (1-Butanol)	ND	688	873	872	1,200	1,600	57.3	54.5	54.5	55.5	2.91
Carbon disulfide	0.558	144	140	184	600	800	23.9	17.4	22.9	21.4	16.4
Carbon tetrachloride	ND	292	269	317	600	800	48.7	33.6	39.6	40.6	18.6
Chlorobenzene	1.95	418	505	491	600	800	69.4	62.8	61.1	64.4	6.76
Chloroform	0.304	402	466	470	600	800	67.0	58.2	58.7	61.3	8.04
1,2-Dichloroethane	ND	462	582	563	600	800	77.1	72.8	70.4	73.4	4.59
1,1-Dichloroethene	ND	214	213	254	600	800	35.7	26.7	31.8	31.4	14.5
Ethyl acetate	ND	1,006	1,219	1,105	1,200	1,600	83.8	76.2	69.1	76.4	9.65
Ethylbenzene	1.25	374	423	431	600	800	62.1	52.7	53.8	56.2	9.22
Ethyl ether	1.36	684	720	675	1,200	1,600	56.9	44.9	42.1	48.0	16.4
Isobutanol (4-Methyl-1-propanol)	ND	ND	ND	ND	1,200	1,600	0.0	0.0	0.0	0.0	NA
Methylene chloride	1.13	187	435	460	600	800	31.0	54.2	57.4	47.5	30.3
Methyl ethyl ketone (2-Butanone)	13.3	714	955	858	1,200	1,600	58.4	58.8	52.8	56.7	5.94
Methyl isobutyl ketone	4.21	1,074	1,309	1,165	1,200	1,600	89.2	81.5	72.5	81.1	10.3
1,1,2,2-Tetrachloroethane	0.908	445	545	520	600	800	74.0	68.0	64.8	69.0	6.73
1,1,2,2-Tetrachloroethane	1.88	535	711	629	600	800	88.9	88.7	78.4	85.3	7.04
Tetrachloroethene	0.614	308	319	356	600	800	51.2	39.8	44.4	45.1	12.7
Toluene	2.02	390	451	456	600	800	64.7	56.2	56.8	59.2	8.06
1,1,1-Trichloroethane	ND	334	328	360	600	800	55.6	41.0	45.0	47.2	16.0
1,1,2-Trichloroethane	0.878	480	620	572	600	800	79.9	77.4	71.4	76.2	5.72
Trichloroethene	1.40	370	403	417	600	800	61.4	50.2	51.9	54.5	11.1
Trichlorofluoroethane	0.416	148	120	179	600	800	24.6	15.0	22.4	20.7	24.5
1,1,2-Trichloro-trifluoroethane	0.231	108	108	185	600	800	17.9	13.4	23.1	18.1	26.7
Vinyl chloride	ND	69.5	57.4	81.0	600	740	11.6	7.8	10.9	10.1	20.3
o- and p-Xylene (d)	2.80	781	879	900	1,200	1,600	64.9	54.8	56.1	58.6	9.40

FOOTNOTES:

a) % Recovery = (amount found in spiked set - amount found at native level)/amount spiked) x 100.
b) Avg = average of the three sets % recovery.
c) %RSD = (Standard deviation / Avg of values) x 100.
d) o- and p-Xylene coelute under the GC conditions specified in Method 8240.
e) Quantitation limits
- Native level determination: 20 to 200 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 40 to 400 µg/L.
- Spiked matrix determination: 100 to 1,000 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 400 to 4,000 µg/L.

TABLE A-9. RESULTS FOR SPIKED SOIL NO. 2 LEACHATES

	Amount Found (µg/L)				Amount Spiked (µg/L)		% Recovery (a)				
Analyte	Native Level	Spiked Set 1	Spiked Set 2	Spiked Set 3	Set 1	Set 2,3	Set 1	Set 2	Set 3	Avg (b)	%RSD (c)
Acetone	42.1	579	726	743	1,200	1,600	44.7	42.8	43.8	43.8	2.25
Acrylonitrile	ND	59.5	595	538	600	800	9.91	74.4	67.3	50.5	70.0
Benzene	52.3	254	379	290	600	800	33.7	40.9	29.7	34.8	16.3
n-Butyl alcohol (1-Butanol)	ND	567	915	691	1,200	1,600	47.2	57.2	43.2	49.2	14.6
Carbon disulfide	0.748	59.8	163	69.9	600	800	9.85	20.3	8.65	12.9	49.5
Carbon tetrachloride	ND	100	236	168	600	800	16.7	29.4	20.9	22.3	29.1
Chlorobenzene	101	317	477	432	600	800	36.1	47.0	41.5	41.5	13.1
Chloroform	0.355	291	521	407	600	800	48.4	65.1	50.9	54.8	16.4
1,2-Dichloroethane	ND	384	621	514	600	800	64.0	77.7	64.3	68.7	11.3
1,1-Dichloroethene	ND	113	266	133	600	800	18.9	33.2	16.7	22.9	39.3
Ethyl acetate	ND	928	1,231	1,150	1,200	1,600	77.3	77.0	71.9	75.4	4.02
Ethylbenzene	13.6	137	221	198	600	800	20.6	25.9	23.1	23.2	11.5
Ethyl ether	3.07	727	797	891	1,200	1,600	60.3	49.6	55.5	55.1	9.72
Isobutanol (4-Methyl-1-propanol)	ND	ND	ND	ND	1,200	1,600	0.0	0.0	0.0	0.0	NA
Methylene chloride	2.08	347	377	180	600	800	57.5	46.8	22.2	42.2	42.9
Methyl ethyl ketone (2-Butanone)	49.9	819	999	1,049	1,200	1,600	64.1	59.3	62.4	61.9	3.94
Methyl isobutyl ketone	25.6	1,068	1,497	1,433	1,200	1,600	86.9	91.9	87.9	88.9	2.99
1,1,2,2-Tetrachloroethane	0.837	221	368	327	600	800	36.6	45.9	40.8	41.1	11.3
1,1,2,2-Tetrachloroethane	2.58	339	480	489	600	800	56.1	59.7	60.8	58.9	4.15
Tetrachloroethene	0.560	74.5	141	126	600	800	12.3	17.5	15.7	15.2	17.4
Toluene	59.8	333	501	436	600	800	45.6	55.2	47.0	49.3	10.5
1,1,1-Trichloroethane	ND	168	341	248	600	800	27.9	42.6	31.0	33.8	22.8
1,1,2-Trichloroethane	ND	376	589	525	600	800	62.7	73.6	65.6	67.3	8.43
Trichloroethene	1.10	197	383	305	600	800	32.6	47.8	38.0	39.4	19.5
Trichlorofluoroethane	ND	59.0	170	54.8	600	800	9.83	21.2	6.85	12.6	60.1
1,1,2-Trichlorotrifluoroethane	ND	25.1	92.7	40.7	600	800	4.19	11.6	5.09	6.95	58.0
Vinyl chloride	ND	39.4	93.8	16.9	600	740	6.57	12.7	2.28	7.17	72.8
o- and p-Xylene (d)	57.9	90.9	90.4	438	1,200	1,600	2.74	2.03	23.8	9.52	130

FOOTNOTES:

a) % Recovery = (amount found in spiked set - amount found at native level)/amount spiked) x 100.

b) Avg = average of the three sets % recovery.

c) %RSD = (Standard deviation / Avg of values) x 100.

d) o- and p-Xylene coelute under the GC conditions specified in Method 8240.

e) Quantitation limits

- Native level determination: 20 to 200 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 40 to 400 µg/L.
- Spiked matrix determination: 100 to 1,000 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 400 to 4,000 µg/L.

TABLE A-10. RESULTS FOR BLANK DEVICE LEACHATES AND SYSTEM BLANKS

	Blank Device Leachates Amount Found (μg/L)		System Blanks Amount Found (μg/L)	
Analyte	Soil 1 Blank	Soil 2 Blank	Blank 1	Blank 2
Acetone	3.50	4.14	17.1	16.6
Acrylonitrile	ND	ND	ND	ND
Benzene	0.846	0.846	1.05	1.24
n-Butyl alcohol (1-Butanol)	ND	ND	ND	ND
Carbon disulfide	ND	ND	ND	ND
Carbon tetrachloride	ND	ND	ND	ND
Chlorobenzene	ND	0.853	ND	ND
Chloroform	ND	0.174	0.208	0.228
1,2-Dichloroethane	ND	ND	ND	ND
1,1-Dichloroethene	ND	ND	ND	ND
Ethyl acetate	ND	ND	ND	ND
Ethylbenzene	1.08	0.645	0.868	0.743
Ethyl ether	0.486	0.323	1.30	1.72
Isobutanol (4-Methyl-1-propanol)	ND	ND	ND	ND
Methylene chloride	1.46	0.762	3.63	2.02
Methyl ethyl ketone (2-Butanone)	8.88	8.68	37.7	37.7
Methyl isobutyl ketone	1.96	1.12	2.77	1.51
1,1,1,2-Tetrachloroethane	0.981	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	1.23	1.14
Tetrachloroethene	ND	ND	0.604	0.877
Toluene	0.847	0.680	0.799	ND
1,1,1-Trichloroethane	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND
Trichloroethene	0.869	1.77	ND	ND
Trichlorofluoroethane	0.313	0.302	0.311	0.336
1,1,2-Trichlorotrifluoroethane (Freon 113)	ND	ND	ND	0.236
Vinyl chloride	ND	ND	ND	ND
o- and p-Xylene	2.51	1.66	ND	2.07

2.2 CALIFORNIA MODEL URBAN SOILS FOR PRECISION AND CLEAN SOIL FOR RUGGEDNESS TESTS

2.2.1 Experimental Procedures

2.2.1.1 Standards Preparation--

Standards were prepared from EPA ampules obtained from the Quality Assurance Materials Bank c/o Northrup Services, Inc., Research Triangle Park, North Carolina.

Additional standards were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, when an EPA Standard was unavailable. A composite stock standard containing 42 volatile organic test compounds at 200 µg/mL was then prepared from the individual dilutions and mixes and was used for all the soil fortifications.

2.2.1.2 Sample Preparation--

Clean soil from a landsite near Lake Chabot Regional Park in Hayward, California, was used for ruggedness test - Soils contaminated with California municipal sludges (soils No. 3 and No. 4) were also used for an additional precision test.

The clean soil was sieved to remove small rocks and twigs. The soil was then spread in a thin layer on a stainless steel tray lined with aluminum foil and placed in a clean 120° C drying oven overnight. The dry soil was then removed and allowed to cool prior to transferring it to several clean amber quart jars. Clean, organic free water was then added to 20 percent by weight and the jars were then sealed. They were then placed on a rotary apparatus and tumbled end-over-end for 12 hours. Afterwards, the clean soil was re-sieved to obtain two particle sizes:

large: 2.34 - 9.5 mm
small: 2.45 mm or less

The separate sized soil samples were then placed in clean amber jars, sealed, and stored in a refrigerator at 4° C.

For the ruggedness tests, 22 grams of the clean soil were weighed into a VOA vial and placed in a refrigerator at 4° C for 1 hour. The VOA vial was then removed and 1 mL of clean water was added. The soil was fortified at the appropriate level by addition of the composite standard spike solution through the vial's septum, followed by brief and moderate agitation. The VOA vial was then returned to the refrigerator for 1 hour to allow interaction between the analytes and the soil prior to ZHE transfer.

For the precision experiments, the chilled contaminated soils (No. 3 and 4) were spiked directly within the ZHE device (with piston up), capped with filter assembly in place and placed in a refrigerator at 4° C for 1 hour prior to addition of the extraction fluid.

2.2.1.3 Zero Headspace Extractor Sample Loading and Operation--

The ZHE devices were assembled and piston adjusted to a height of 1/2 inch from the top of the cylinder. (This facilitated loading of the device with sample while keeping headspace to a minimum.)

The filter assembly and top sealing flange were then quickly secured in place with the liquid valve in the closed position. A second ZHE was used as an extraction fluid reservoir. A 1/8 inch diameter Teflon line was used to couple the ZHEs via their respective liquid inlet/outlet valves. Applying positive pressure to the reservoir's piston forced the extraction fluid into the ZHE device containing the soil sample. The pressurizing valve of the ZHE must be kept open for this step to permit free piston movement without back pressure.

Following addition of the extraction fluid, the inlet valve is closed and the vessel pressurized to 10-15 psi with a nitrogen gas line connected to a two stage regulator. The ZHE device was then placed on a rotary apparatus for 5 minutes. Next, the liquid valve was momentarily opened and closed to relieve any accumulated gas pressure. The device was then slowly repressurized to 10-15 psi. This was done with the liquid inlet valve briefly opened to force any gas present to be expelled. The ZHE device was then returned to the rotary apparatus and tumbled end-over-end at 30 rpms for the required extraction time.

When the extraction period was over, the ZHE was removed and the device was checked to determine if any pressure loss had occurred. The leachate was then transferred to a small evacuated Tedlar bag by applying pressure to the ZHE's piston. Pressure was always applied gradually, initially 10-15 psi and then gradually increased in 5 psi increments to a maximum of 50 psi. This helped to prevent premature filter caking or possible breakage.

After the initial transfer, several VOA vials were filled to the top with the collected leachate, capped and then stored in a refrigerator at 4° C until analyzed.

2.2.1.4 Analytical Instrumentation and Analysis--

All analyses for method 1312 precision and ruggedness testing were carried out on a Varian 3400 - Finnigan 4021 GC/MS system. The data system consisted of a NOVA IV computer, 70 Mbyte Winchester drive and INCOS version 5.5 software.

Instrumental Conditions Were:

Injector: 200° C. (1:15 split ratio)

Column: 30 m X 0.32 mm DB-624 fused silica capillary

Oven Program: -10° C (1 min) ⟶ 30°C at 15° C/min
30° C ⟶ 125° C(5 min) at 6° C/min, with 5 min hold at 125° C

Transfer Line: 250° C

Analysis of the leachates was carried out according to the current SW-846 Method 8260 protocol.

TABLE A-11. SURROGATE RECOVERIES FOR METHOD 1312 PRECISION AND RUGGEDNESS TESTING FOR VOLATILE ORGANIC TEST COMPOUNDS

Leachate	Toluene-d_8	BFB	Dichloroethane-d_4
Native Soil 1	91.9%	96.3%	90.0%
Native Soil 1 Matrix Spike	92.4%	89.5%	87.7%
Spiked Soil 1, Set 1	99.3%	106%	103%
Spiked Soil 1, Set 2	100%	100%	102%
Spiked Soil 1, Set 3	97.9%	99.2%	101%
Native Soil 2	90.0%	87.2%	80.5%
Native Soil 2, Matrix Spike	91.8%	100%	94.2%
Spiked Soil 2, Set 1	97.8%	101%	107%
Spiked Soil 2, Set 2	98.7%	103%	105%
Spiked Soil 2, Set 3	89.1%	95.3%	97.2%
Method Blank 1	94.0%	99.7%	97.1%
Method Blank 2	90.3%	96.2%	91.9%

TABLE A-12. MATRIX SPIKE RESULTS FOR NATIVE SOIL LEACHATES

	Amount Found (µg/L)			
Analyte	Native Level	Matrix Spike	Amount Spiked (µg/L)	Matrix Spike % Recovery
SOIL NO. 1				
Benzene	1.18	47.2	50.0	92.0%
Chlorobenzene	ND	51.0	50.0	102%
1,1-Dichloroethene	0.146	47.7	50.0	95.2%
Toluene	2.02	52.2	50.0	100%
Trichloroethene	1.40	48.1	50.0	93.4%
SOIL NO. 2				
Benzene	52.3	43.4	50.0	-17.8%
Chlorobenzene	101	155	50.0	110%
1,1-Dichloroethene	0.313	46.7	50.0	92.8%
Toluene	59.8	115	50.0	110%
Trichloroethene	1.10	45.6	50.0	88.7%

TABLE A-13. METHOD 1312 REPLICATES DATA FOR CONTAMINATED SOIL NO. 3 FORTIFIED WITH VOLATILE COMPOUNDS

Compound Name	Sets 1-6 Spike Amt. mg/kg	Blank	Percent Recoveries (%)							
			Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Avg.	%RSD
Chloromethane	2.0	n.d.	24			28	17	62	32.8	61.1
Bromomethane	2.0	n.d.	44			26	20	64	36.5	51.5
Vinyl chloride	2.0	n.d.	22			19	12	47	25.0	61.0
Chloroethane	2.0	n.d.	68			31	23	71	48.3	51.4
Methylene chloride	2.0	6	59			47	28	74	52.0	37.4
Acetone	2.0	9	129			103	126	106	116.0	11.5
Carbon disulfide	2.0	2	41			25	19	61	36.5	51.5
1,1-Dichloroethene	2.0	n.d.	35			23	15	55	32.0	54.5
1,1-Dichloroethane	2.0	n.d.	53			37	26	76	48.0	45.2
trans-1,2-dichloroethene	2.0	n.d.	44			30	20	65	39.8	49.1
Chloroform	2.0	2	48			53	58	88	61.8	29.1
1,2-Dichloroethane	2.0	n.d.	60	74	57	40	34	85	58.3	33.3
2-Butanone	2.0	n.d.	56	79	54	62	75	116	73.7	31.3
1,1,1-Trichloroethane	2.0	n.d.	40	53	39	27	20	65	40.7	40.4
Carbon tetrachloride	2.0	n.d.	34	44	34	26	18	61	36.2	41.4
Bromodichloromethane	2.0	n.d.	59	78	59	39	34	83	58.7	33.8
1,1,2,2-Tetrachloroethane	2.0	n.d.	61	68	57	51	52	95	64.0	25.7
1,2-Dichloropropane	2.0	n.d.	59	76	56	44	30	79	57.3	32.6
cis-1,3-Dichloropropene	2.8	n.d.	71	81	68	45	44	103	68.7	32.6
Trichloroethene	2.0	n.d.	39	48	36	27	19	64	38.8	40.9
Dibromochloromethane	2.0	n.d.	53	65	51	42	39	86	56.0	30.9
1,1,2-Trichloroethane	2.0	n.d.	59	75	62	45	42	87	61.7	28.0
Benzene	2.0	n.d.	53	67	50	34	24	71	49.8	36.7
trans-1,3-Dichloropropene	2.3	n.d.	56	67	54	33	30	79	53.2	35.8
Bromoform	2.0	n.d.	49	56	45	47	44	91	55.3	32.5
4-Methyl-2-pentanone	2.0	3	60	71	48	42	40	89	58.3	32.6
Tetrachloroethene	2.0	n.d.	24	30	23	19	14	47	26.2	44.0
Toluene	2.0	n.d.	47	58	45	31	25	68	45.7	35.2
Chlorobenzene	2.0	n.d.	44	52	42	32	28	67	44.2	32.0
Ethylbenzene	2.0	n.d.	37	47	36	26	21	58	37.5	36.1
Styrene	2.0	n.d.	36	40	37	28	25	68	39.0	39.3
p-Xylene	2.0	n.d.	41	44	36	25	20	57	37.2	38.1
o-Xylene	2.0	n.d.	41	48	41	31	26	66	42.2	33.4
1,4-Dichlorobenzene	2.0	n.d.	27	30	27	22	21	50	29.5	35.9
Trichlorofluoromethane	2.0	n.d.	25			30	18	41	28.5	34.0
Acrylonitrile	11.0	n.d.	72			51	55	19	49.3	44.9
n-Butanol	20.0	n.d.	76	90	57	70	79	21	65.5	37.2
Ethyl acetate	11.0	n.d.	55			37	0	0	23.0	119.8
Ethyl ether	11.0	n.d.	45			43	41	20	37.3	31.2
Isobutanol	20.0	n.d.	69	80	62	68	76	16	61.8	37.7
1,1,2-Trichlorotrifluoroethane (Freon 113)	2.0	n.d.	13			18	12	43	21.5	67.8
1,1,1,2-Tetrachloroethane	2.0	n.d.	50	58	48	38	33	78	50.8	31.5

NOTE: All values in the table above have been blank corrected. Blank entries in the table indicate that a reliable quantitation could not be made due to a carryover problem involving the first internal standard.

TABLE A-14. METHOD 1312 REPLICATES DATA FOR CONTAMINATED SOIL NO. 4 FORTIFIED WITH VOLATILE COMPOUNDS

Compound Name	Sets 1-6 Spike Amt. mg/kg	Blank	Percent Recoveries (%)						
			Set 1	Set 2	Set 3	Set 4	Set 5	Avg.	%RSD
Chloromethane	2.2	n.d.	16		15	13	22	16.5	23.5
Bromomethane	2.2	n.d.	27		14	14	23	19.5	33.6
Vinyl chloride	2.0	n.d.	11		11	9	16	11.8	25.4
Chloroethane	2.2	n.d.	38		19	16	28	25.3	39.3
Methylene chloride	2.0	5	41		40	28	40	37.3	16.6
Acetone	2.0	55	30		34	21	0	21.3	71.4
Carbon disulfide	2.0	n.d.	28		16	15	26	21.3	31.5
1,1-Dichloroethene	2.0	n.d.	21		14	12	20	16.8	26.4
1,1-Dichloroethane	2.0	n.d.	33		21	20	32	26.5	26.2
trans-1,2-Dichloroethene	2.0	n.d.	27		17	16	26	21.5	27.0
Chloroform	2.0	n.d.	32		32	50	69	45.8	38.6
1,2-Dichloroethane	2.0	n.d.	41	67	26	33	39	41.2	37.8
2-Butanone	2.0	n.d.	40	65	36	41	21	40.6	39.0
1,1,1-Trichloroethane	2.0	n.d.	31	41	17	17	25	26.2	38.8
Carbon tetrachloride	2.0	n.d.	28	35	16	16	25	24.0	34.0
Bromodichloromethane	2.0	n.d.	46	69	26	32	39	42.4	39.3
1,1,2,2-Tetrachloroethane	2.0	n.d.	48	66	45	58	51	53.6	15.8
1,2-Dichloropropane	2.0	n.d.	43	65	23	28	35	38.8	42.4
cis-1,3-Dichloropropene	2.6	n.d.	51	74	31	47	47	50.0	30.9
Trichloroethene	2.0	n.d.	30	38	17	18	25	25.5	34.1
Dibromochloromethane	2.0	n.d.	40	57	30	41	41	41.8	23.2
1,1,2-Trichloroethane	2.0	n.d.	44	66	34	44	44	46.4	25.4
Benzene	2.0	n.d.	37	54	19	23	34	33.4	41.1
trans-1,3-Dichloropropene	2.3	n.d.	41	59	20	30	34	36.6	39.5
Bromoform	2.0	n.d.	38	51	38	50	46	44.6	14.1
4-Methyl-2-pentanone	2.0	6	37	67	29	39	27	39.6	40.3
Tetrachloroethene	2.0	n.d.	21	24	13	15	20	18.6	24.2
Toluene	2.0	n.d.	36	49	19	24	29	31.4	37.2
Chlorobenzene	2.0	n.d.	36	45	23	29	32	33.0	24.9
Ethylbenzene	2.0	n.d.	31	38	18	22	27	27.2	28.6
Styrene	2.0	n.d.	31	35	21	27	29	28.6	18.1
p-Xylene	2.0	n.d.	31	37	17	21	26	26.4	30.0
o-Xylene	2.0	n.d.	39	43	22	27	34	33.0	26.0
1,4-Dichlorobenzene	2.0	n.d.	23	26	18	23	23	22.6	12.7
Trichlorofluoromethane	2.0	n.d.	21		23	10	25	19.8	33.9
Acrylonitrile	11.0	n.d.	50		50	52	55	51.8	4.6
n-Butanol	20.0	n.d.	67	91	67	70	70	73.0	13.9
Ethyl acetate	11.0	n.d.	22		22			11.0	115.5
Ethyl ether	11.0	n.d.	39		39	37	53	42.0	17.6
Isobutanol	20.0	n.d.	68	86	68	72	86	76.0	12.2
1,1,2-Trichlorotrifluoroethane (Freon-113)	2.0	n.d.	18		12	12	19	15.3	24.8
1,1,1,2-Tetrachloroethane	2.0	n.d.	38	50	26	33	37	36.8	23.8

NOTE: All values in the table above have been blank corrected. Blank entries in the table indicate that a reliable quantitation could not be made due to a carryover problem involving the first internal standard.

TABLE 15. SURROGATE RECOVERIES FOR METHOD 1312 PRECISION AND RUGGEDNESS TESTING FOR VOLATILE ORGANIC TEST COMPOUNDS

SU1: d_4-1,2-Dichloroethane
SU2: d_8-Toluene
SU3: p-Bromofluorobenzene

Ruggedness Tests	SU1	SU2	SU3
Experiment 1	106	97	96
Experiment 2	101	104	102
Experiment 3	108	98	100
Experiment 4	90	101	96
Experiment 5	104	94	101
Experiment 6	107	104	105
Experiment 7	85	95	95
Experiment 8	102	100	101
Precision Sets			
Contaminated soil No. 3			
Unfortified	87	93	92
Set 1	93	102	101
Set 2	*	101	100
Set 3	*	102	101
Set 4	92	99	100
Set 5	90	98	103
Set 6	91	99	99
Contaminated soil No. 4			
Unfortified	90	95	93
Set 1	85	100	100
Set 2	*	100	104
Set 3	0	0	0
Set 4	90	98	100
Set 5	95	102	102
Set 6	90	99	102

An asterisk(*) in the table above indicates that a reliable quantitation could not be made due to a carry-over problem involving the first internal standard.

APPENDIX B

INITIAL CHARACTERIZATIONS OF THE SOILS AND SLUDGES USED FOR METHOD 1312 PRECISION AND RUGGEDNESS TESTS

1.0 INTRODUCTION

1.1 The various types of soil and sludge contaminated soil samples used for the Method 1312 precision and ruggedness study need to be characterized for their organic and inorganic contents in order that appropriate spiking levels of the various target analytes can be determined. The initial characterization data on these samples are presented in this appendix.

1.2 Since Method 1312 is designed to simulate a real world scenario under natural environmental conditions at waste disposal sites, the type of samples to be analyzed by this method could contain various types of waste in addition to soil. Therefore, in order to perform a complete evaluation of this method, soil samples contaminated with various types of waste needed to be used. In addition to the two Superfund site soils which should contain priority pollutants, municipal sludges from two San Francisco Bay area sites were also collected and used for this study. These sludges were used in two ways; (1) they were mixed with clean soil to make composites which are considered to simulate contaminated soils from typical municipal sources (i.e., California Model Urban Soils); and (2) they were used as they are to simulate a worse scenario case, to obtain additional precision data which are also presented in this appendix.

2.0 RESULTS AND DISCUSSION

2.1 For the initial characterizations of the two soils and two sludges, the analysis results were summarized below and the data presented in Tables 1 thru 10.

2.2 Soil and sludge samples were extracted and analyzed according to current SW-846 method protocols. Soils were prepared as low level extracts while the sludges underwent medium level extractions. Cleanup (with sulfur removal) was required prior to Pesticides and PCBs analysis. Of the samples characterized, Soil No. 2 contained the highest levels of contamination. The volatile analysis (Method 8240) identified several aromatic hydrocarbons including toluene, chlorobenzene and xylenes at concentrations of 300 to 400 ppm while, the semivolatile analysis (Method 8270) identified a number of PAH's at the 3 to 5 ppm level. Both sludge samples contained aliphatic hydrocarbons each totaling 50 ppm while acetone was found at 120 ppm in Sludge No. 1. The remaining other soil sample was relatively uncontaminated. No pesticides or PCBs were found at or above the reported method detection limits for any of the samples.

2.3 Similarly, Atomic Absorption and ICAP did not indicate any exceptionally high levels of toxic metals except for lead (390 ppm) and chromium (80 ppm) which were found in the contaminated Soil No. 2.

2.4 Due to the large amounts of sulfur present (particularly in the sludges), it was not always possible to quantitatively remove all of the sulfur interference and, in one instance, the remaining sulfur present may have adversely affected the electron capture detector response and pesticide matrix spike recovery. However, acceptable recoveries were obtained for the duplicate spike and since no pesticides or PCB's were found in the unspiked sample, a repeat analysis was considered unnecessary.

2.5 QA/QC criteria for each analytical method were strictly adhered to and overall results were very favorable. Matrix spikes and surrogate recoveries were particularly superior in this regard.

2.6 For the Semi-volatile Soil Matrix Spike analysis, 1,2,4-Trichlorobenzene was high for both the Matrix Spike and Matrix Spike Duplicate, however, this same compound was found at a high level (8.5 ppm) in the unspiked sample.

2.7 The soil and sludge initial characterization results are presented in Tables 1 through 10 which follow.

* Table 1.	Volatile Organic Results
* Table 2.	Semi volatile Organic Results
* Table 3.	Pesticide and PCB Results
* Table 4.	Metals Results
* Table 5.	Tentatively Identified Compounds Results
* Table 6.	General Chemistry Results
* Table 7.	Volatile Organics Matrix Spike Results
* Table 8.	Semi volatile Organic Matrix Spike Results
* Table 9.	Pesticide and PCB Matrix Spike Results
* Table 10.	Metals Matrix Spike Results

2.8 Additional precision results performed on the two sludges were presented in Tables 11 and 12. The unspiked Sludge 1 leachate (Native Level column in Table 11) had acetone at a concentration above the quantitation limit. Thee average percent recoveries for the target analytes in the spiked sludge leachates were also variable, ranging from 7 to 76 percent, with isobutanol not detected in any of the leachates. Nineteen of the twenty-eight target analytes (68 percent) had %RSDs below 25 percent. The Sludge 2 unspiked leachate (Native Level in Table 12) also had levels of acetone above the quantitation limit. The average percent recovery of all target components in the spiked sludge leachates ranged from 10 to 79 percent, and isobutanol was not detected. Twenty-six of the twenty-eight target analytes (93 percent) had RSDs of less than 25 percent.

TABLE 1. VOLATILE ORGANIC RESULTS

	Soil No. 1	Soil No. 2	Sludge No. 1	Sludge No. 2	Method Blank
8240 Compounds	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Chloromethane	<10	<5000	<50	<50	<10
Bromomethane	<10	<5000	<50	<50	<10
Vinyl chloride	<10	<5000	<50	<50	<10
Chloroethane	<10	<5000	<50	<50	<10
Methylene chloride	6	<2500	<25	<25	<5
Trichlorofluoromethane	<5	<2500	<25	<25	<5
1,1-Dichloroethene	<5	<2500	<25	<25	<5
1,1-Dichloroethane	<5	<2500	<25	<25	<5
trans-1,2-Dichloroethene	<5	<2500	<25	<25	<5
Chloroform	<5	<2500	<25	<25	<5
1,2-Dichloroethane	<5	<2500	<25	<25	<5
1,1,1-Trichloroethane	<5	<2500	<25	<25	<5
Carbon tetrachloride	<5	<2500	<25	<25	<5
Bromodichloromethane	<5	<2500	<25	<25	<5
1,2-Dichloropropane	<5	<2500	<25	<25	<5
trans-1,3-Dichloropropene	<5	<2500	<25	<25	<5
Trichloroethene	<5	<2500	<25	<25	<5
Benzene	<5	<2500	<25	<25	<5
Dibromochloromethane	<5	<2500	<25	<25	<5
1,1,2-Trichloroethane	<5	<2500	<25	<25	<5
cis-1,3-Dichloropropene	<5	<2500	<25	<25	<5
2-Chloroethylvinylether	<10	<5000	<50	<50	<10
Bromoform	<5	<2500	<25	<25	<5
1,1,2,2-Tetrachloroethane	<5	<2500	<25	<25	<5
Tetrachloroethene	<5	<2500	<25	40	<5
Toluene	<5	390000	35	<25	<5
Chlorobenzene	<5	310000	<25	<25	<5
Ethylbenzene	<5	50000	<25	<25	<5
Dichlorobenzenes	<5	<2500	65	150	<5
Acetone	39	<10000	121000	820	<20
Carbon disulfide	<20	<10000	<100	<100	<20
2-Butanone	<20	58000	420	185	<20

(continued)

TABLE 1. (Continued)

8240 Compounds	Soil No. 1 µg/kg	Soil No. 2 µg/kg	Sludge No. 1 µg/kg	Sludge No. 2 µg/kg	Method Blank µg/kg
Vinyl acetate	<20	<10000	<100	<100	<20
4-Methyl-2-pentanone	<20	25000	<100	<100	<20
2-Hexanone	<20	<10000	<100	<100	<20
Styrene	<5	<2500	<25	55	<5
Xylene	<5	290000	30	<25	<5
Date Analyzed	10/7/88	10/7/88	10/7/88	10/7/88	10/7/88
Surrogates	Percent Recoveries (%)				
1,2-Dichloroethane-d_4	98	105	100	97	104
Toluene-d_8	102	107	105	100	101
p-Bromofluorobenzene	100	112	93	97	105

TABLE 2. SEMI VOLATILE ORGANIC RESULTS

8270 Compounds	Soil No. 1 µg/kg	Soil No. 2 µg/kg	Sludge No. 1 µg/kg	Sludge No. 2 µg/kg	Method Blank µg/kg
Fluoranthene	<330	4800	<7100	<7400	<330
Pyrene	<330	4500	<7100	<7400	<330
Butyl benzyl phthalate	<330	4700	<7100	<7400	<330
3,3'-Dichlorobenzidine	<1300	<6700	<29000	<29000	<1300
Benzo(a)anthracene	<330	2700	<7100	<7400	<330
bis(2-Ethylhexyl)-phthalate	<330	17000	<7100	<7400	<330
Chrysene	<330	3300	<7100	<7400	<330
Di-n-octyl phthalate	<330	<1700	<7100	<7400	<330
Benzo(b)fluoranthene	<330	3300	<7100	<7400	<330
Benzo(k)fluoranthene	<330	<1700	<7100	<7400	<330
Benzo(a)pyrene	<330	2500	<7100	<7400	<330
Indeno(1,2,3-cd)pyrene	<330	<1700	<7100	<7400	<330
Dibenzo(a,h)anthracene	<330	<1700	<7100	<7400	<330
Benzo(g,h,i)perylene	<330	1700	<7100	<7400	<330
Benzyl alcohol	<3300	<17000	<71000	<74000	<3300
2-Methyl phenol	<330	551	<7100	<7400	<330
4-Methyl phenol	<330	724	<7100	<7400	<330
Benzoic acid	<3300	400	<71000	<74000	<3300
4-Chloroaniline	<3300	<17000	<71000	<74000	<3300
2-Methylnaphthalene	<330	1112	<7100	<7400	<330
2,4,5-Trichlorophenol	<330	<1700	<7100	<7400	<330
2-Nitroaniline	<3300	<17000	<71000	<74000	<3300
3-Nitroaniline	<3300	<17000	<71000	<74000	<3300
Dibenzofuran	<330	<1700	<7100	<7400	<330
2,6-Dinitrotoluene	<330	<1700	<7100	<7400	<330
4-Nitroaniline	<3300	<17000	<71000	<74000	<3300
Date Analyzed	10/10/88	10/10/88	10/3/88	10/3/88	10/3/88
Date Extracted	10/4/88	10/4/88	10/3/88	10/3/88	10/3/88

Surrogates	Percent Recovery (%)				
2-Fluorophenol	55	45	63	62	76
Phenol-d_5	62	50	62	62	74
Nitrobenzene-d_5	61	85	64	67	77
2-Fluorobiphenyl	65	55	68	69	80
2,4,6-Tribromophenol	64	20	89	89	87
p-Terphenyl-d_{14}	69	60	70	72	90

(continued)

TABLE 2. (CONTINUED)

8270 Compounds	Soil No. 1 µg/kg	Soil No. 2 µg/kg	Sludge No. 1 µg/kg	Sludge No. 2 µg/kg	Method Blank µg/kg
Phenol	<330	<1700	<7100	<7400	<330
bis(2-Chloroethyl)ether	<330	<1700	<7100	<7400	<330
2-Chlorophenol	<330	<1700	<7100	<7400	<330
1,3-Dichlorobenzene	<330	<1700	<7100	<7400	<330
1,4-Dichlorobenzene	<330	<1700	<7100	<7400	<330
1,2-Dichlorobenzene	<330	<1700	<7100	<7400	<330
bis(2-Chloroisopropyl)-ether	<330	<1700	<7100	<7400	<330
N-Nitroso-di-n-propylamine	<330	<1700	<7100	<7400	<330
Hexachloroethane	<330	<1700	<7100	<7400	<330
Nitrobenzene	<330	<1700	<7100	<7400	<330
Isophorone	<330	7000	<7100	<7400	<330
2-Nitrophenol	<330	<1700	<7100	<7400	<330
2,4-Dimethylphenol	<330	<1700	<7100	<7400	<330
bis(2-Chloroethoxy) methane	<330	<1700	<7100	<7400	<330
2,4-Dichlorophenol	<330	<1700	<7100	<7400	<330
1,2,4-Trichlorobenzene	<330	8500	<7100	<7400	<330
Naphthalene	<330	1800	<7100	<7400	<330
Hexachlorobutadiene	<330	<1700	<7100	<7400	<330
4-Chloro-3-methylphenol	<330	<1700	<7100	<7400	<330
Hexachlorocyclo-pentadiene	<330	<1700	<7100	<7400	<330
2,4,6-Trichlorophenol	<330	<1700	<7100	<7400	<330
2-Chloronaphthalene	<330	<1700	<7100	<7400	<330
Dimethyl phthalate	<330	<1700	<7100	<7400	<330
Acenaphthylene	<330	<1700	<7100	<7400	<330
Acenaphthene	<330	<1700	<7100	<7400	<330
2,4-Dinitrophenol	<3300	<17000	<71000	<74000	<3300
4-Nitrophenol	<3300	<17000	<71000	<74000	<3300
2,4-Dinitrotoluene	<330	<1700	<7100	<7400	<330
2,6-Dinitrotoluene	<330	<1700	<7100	<7400	<330
Diethyl phthalate	<330	<1700	<7100	<7400	<330
4-Chlorophenyl-phenylether	<330	<1700	<7100	<7400	<330
Fluorene	<330	<1700	<7100	<7400	<330
4,6-Dinitro-2-methyl-phenol	<3300	<17000	<71000	<74000	<3300
N-Nitrosodiphenylamine	<330	<1700	<7100	<7400	<330
4-Bromophenyl phenyl-ether	<330	<1700	<7100	<7400	<330

(continued)

TABLE 2. (CONTINUED)

	Soil No. 1	Soil No. 2	Sludge No. 1	Sludge No. 2	Method Blank
8270 Compounds	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg
Hexachlorobenzene	<330	<1700	<7100	<7400	<330
Pentachlorophenol	<3300	<17000	<71000	<74000	<3300
Phenanthrene	<330	4100	<7100	<7400	<330
Anthracene	<330	<1700	<7100	<7400	<330
Di-n-Butyl phthalate	<330	<1700	<7100	<7400	<330

TABLE 3. PESTICIDES AND PCBs RESULTS

Pesticides and PCBs	Soil No. 1 μg/kg	Soil No. 2 μg/kg	Sludge No. 1 μg/kg	Sludge No. 2 μg/kg	Method Blank μg/kg
Alpha BHC	<8	<81	<16	<16	<8
Beta BHC	<8	<81	<16	<16	<8
Gamma BHC	<8	<81	<16	<16	<8
Delta BHC	<8	<81	<16	<16	<8
Heptachlor	<8	<81	<16	<16	<8
Aldrin	<8	<81	<16	<16	<8
Heptachlor Epoxide	<8	<81	<16	<16	<8
Endosulfan I	<8	<81	<16	<16	<8
Dieldrin	<16	<160	<32	<32	<16
4,4'-DDE	<16	<160	<32	<32	<16
Endrin	<16	<160	<32	<32	<16
Endosulfan II	<16	<160	<32	<32	<16
4,4'-DDO	<16	<160	<32	<32	<16
Endosulfan Sulfate	<16	<160	<32	<32	<16
4,4,-DDT	<16	<160	<32	<32	<16
Endrin Aldehyde	<16	<160	<32	<32	<16
Endrin Ketone	<16	<160	<32	<32	<16
Methoxychlor	<80	<800	<160	<160	<80
Chlordane	<80	<800	<160	<160	<80
Toxaphene	<160	<1600	<330	<330	<160
Aroclor-1016	<81	<810	<160	<160	<81
Aroclor-1221	<81	<810	<160	<160	<81
Aroclor-1232	<81	<810	<160	<160	<81
Aroclor-1242	<81	<810	<160	<160	<81
Aroclor-1248	<81	<810	<160	<160	<81
Aroclor-1254	<160	<1600	<330	<330	<160
Aroclor-1260	<160	<1600	<330	<330	<160
Date Extracted:	10/4/88	10/4/88	10/3/88	10/3/88	10/4/88
Date Analyzed:	10/13/88	10/13/88	10/14/88	10/14/88	10/13/88

Surrogates	Percent Recoveries (%)				
DiButyl Chlorendate:	114	0	57	69	126

(continued)

TABLE 3. (Continued)

Pesticides and PCBs	Method Blank µg/kg
Alpha BHC	<11
Beta BHC	<11
Gamma BHC	<11
Delta BHC	<11
Heptachlor	<11
Aldrin	<11
Heptachlor Epoxide	<11
Endosulfan I	<11
Dieldrin	<23
4,4'-DDE	<23
Endrin	<23
Endosulfan II	<23
4,4'-DDD	<23
Endosulfan Sulfate	<23
4'4'-DDT	<23
Endrin Aldehyde	<23
Endrin Ketone	<23
Methoxychlor	<110
Chlordane	<110
Toxaphene	<230
Aroclor-1016	<110
Aroclor-1221	<110
Aroclor-1232	<110
Aroclor-1242	<110
Aroclor-1248	<110
Aroclor-1254	<230
Aroclor-1260	<230
Date Extracted:	10/3/88
Date Analyzed:	10/14/88

Surrogates	
DiButyl Chlorendate:	73

TABLE 4. METALS RESULTS

Parameter	EPA Method	Soil No. 1 mg/kg	Soil No. 2 mg/kg	Sludge No. 1 mg/kg	Sludge No. 2 mg/kg	Method Blank mg/L
Aluminum	6010	12000	8200	110	190	<0.05
Antimony	7041	<1	<1	<1	<1	<0.01
Arsenic	7060	4.8	3	<1	<1	<0.01
Barium	6010	47	110	9.6	9.6	<0.01
Beryllium	6010	<1	<1	<1	<1	<0.01
Cadmium	6010	<1	<1	<1	<1	<0.01
Calcium	6010	4100	10000	830	500	0.31
Chromium	6010	12	82	1	1.6	<0.01
Cobalt	6010	5.9	5.7	<1	<1	<0.01
Copper	6010	16	22	9.5	11	<0.01
Iron	6010	10000	12000	1800	390	<0.01
Lead	6010	<5	390	<5	<5	<0.05
Magnesium	6010	2200	3500	260	240	<0.05
Manganese	6010	110	360	27	3.2	<0.01
Nickel	6010	7.2	13	1.9	2.1	<0.01
Selenium	7740	<1	<1	<1	<1	<0.01
Silver	6010	<1	<1	1.7	1	<0.01
Sodium	6010	1200	250	1100	1400	0.2
Thallium	7841	<1	<1	<1	<1	<0.01
Vanadium	6010	41	11	<1	<1	<0.01
Zinc	6010	22	100	81	27	0.033

TABLE 5. TENTATIVELY IDENTIFIED COMPOUNDS

Parameter	Soil No. 1 µg/kg*	Soil No. 2 µg/kg*	Sludge No. 1 µg/kg*	Sludge No. 2 µg/kg*
Dimethyl disulfide	<40	<170	290	<740
Hexanal	<40	<170	130	<740
Aliphatic hydrocarbons	800	270,000	44,000	53,000
Propyl cyclohexane	<40	9,000	82	<740
Trimethyl bicycloheptane	<40	<720	130	<740
Dimethyl octadienol acetate	<40	<720	280	<740
Trimethyl benzene	<40	38,000	140	110
Ethenyl dimethyl cyclohexane	<40	<170	2,000	1,000
Methyl methyl ethyl benzene	<40	<170	150	130
Decahydronaphthalene	<40	<170	210	220
Ethyl methyl benzene	<40	19,000	<740	<740
Methyl cyclohexane	<40	22,000	<740	<740
Diethyl benzene	<40	14,000	<740	<740
Tetramethyl pentanone	<40	18,000	<740	<740
Molecular sulfur	460	<170	<740	<740
Tetradecanoic acid	<40	<170	27,000	24,000
Ethyl hexyl adipate	470	<170	<740	<740
Trichlorotoluene	<40	3,400	<740	<740
Trichloro-chloromethyl benzene	<40	1,800	<740	<740
Dimethyl ethyl methylpropanediyl propanoate	<40	21,000	<740	<740
bis(methylpentyl)phthalate isomers	<40	40,000	<740	<740
Dichloro trichloromethyl benzene	<40	21,000	<740	<740
bis(hydroxyethyl)dodecanamide	<40	<170	7,700	7,300
Decahydromethyl naphthalene	<40	<170	<740	130

*Approximate quantitation based on comparison of the reconstructed ion chromatogram of compound to the nearest internal standard; assume response factor of 1.

TABLE 6. GENERAL CHEMICAL RESULTS

		Soil No. 1	Soil No. 2	Sludge No. 1	Sludge No. 2
Soil Appraisal Analysis:					
% of sample passing 2 mm screen					
Gravel	>5.00	0.0	11.9	ND	ND
	2.0-5.0	0.0	16.7	ND	ND
Sand	1.0-2.0	0.0	6.0	ND	ND
	0.5-1.0	0.2	11.4	ND	ND
	0.05-0.5	33.4	46.2	ND	ND
Silt	0.002-0.05	58.0	22.0	ND	ND
Clay	0-0.002	8.4	14.4	ND	ND
Classification:		Silt Loam	Sandy Loam	ND	ND
Moisture, %		23	25	94	96
pH, units of pH		6.9	7.0	6.3	5.6
TOX (mg/L)		<5	2190	282	38

ND - Not determined

TABLE 7. VOLATILE ORGANIC MATRIX SPIKE RESULTS

	Soil No. 1 Spike	Soil No. 2 Dup Spike	Sludge No. 1 Spike	Sludge No. 2 Dup Spike
624 Compounds	% Recov	% Recov	% Recov	% Recov
Chloromethane	NS	NS	NS	NS
Bromomethane	NS	NS	NS	NS
Vinyl chloride	NS	NS	NS	NS
Chloroethane	NS	NS	NS	NS
Methylene chloride	NS	NS	NS	NS
Trichlorofluoromethane	NS	NS	NS	NS
1,1-Dichloroethene	102	104	106	102
1,1-Dichloroethane	NS	NS	NS	NS
trans-1,2-Dichloroethene	NS	NS	NS	NS
Chloroform	NS	NS	NS	NS
1,2-Dichloroethane	NS	NS	NS	NS
1,1,1-Trichloroethane	NS	NS	NS	NS
Carbon tetrachloride	NS	NS	NS	NS
Bromodichloromethane	NS	NS	NS	NS
1,2-Dichloropropane	NS	NS	NS	NS
trans-1,3-Dichloropropene	NS	NS	NS	NS
Trichloroethene	100	100	98	102
Benzene	112	114	110	113
Dibromochloromethane	NS	NS	NS	NS
1,1,2-Trichloroethane	NS	NS	NS	NS
cis-1,3-Dichloropropene	NS	NS	NS	NS
2-Chloroethylvinylether	NS	NS	NS	NS
Bromoform	NS	NS	NS	NS
1,1,2,2-Tetrachloroethane	NS	NS	NS	NS
Tetrachloroethene	NS	NS	NS	NS
Toluene	112	110	110	122
Chlorobenzene	110	110	106	108
Ethylbenzene	NS	NS	NS	NS
Dichlorobenzenes	NS	NS	NS	NS
Date Analyzed:	10/7/88	10/7/88	10/7/88	10/7/88

Surrogates	Percent Recoveries (%)			
1,2-Dichloroethane-d_4	101	104	99	96
Toluene-d_8	103	102	104	102
p-Bromofluorobenzene	101	97	93	96

TABLE 8. SEMI VOLATILE ORGANIC MATRIX SPIKE RESULTS

8270 Compounds	Soil No. 1 Spike % Recov	Soil No. 2 Dup Spike % Recov	Sludge No. 1 Spike % Recov	Sludge No. 2 Dup Spike % Recov
Phenol	53	55	46	40
bis(2-chloroethyl)ether	NS	NS	NS	NS
2-Chlorophenol	52	53	49	44
1,3-Dichlorobenzene	NS	NS	NS	NS
1,4 Dichlorobenzene	45	51	50	47
1,2-Dichlorobenzene	NS	NS	NS	NS
bis(2-chloroisopropyl)ether	NS	NS	NS	NS
N-Nitroso-di-n-propylamine	78	84	54	49
Hexachloroethane	NS	NS	NS	NS
Nitrobenzene	NS	NS	NS	NS
Isophorone	NS	NS	NS	NS
2-Nitrophenol	NS	NS	NS	NS
2,4-Dimethylphenol	NS	NS	NS	NS
bis(2-chloroethoxy)methane	NS	NS	NS	NS
2,4-Dichlorophenol	NS	NS	NS	NS
1,2,4-Trichlorobenzene	168	287	58	54
Naphthalene	NS	NS	NS	NS
Hexachlorobutadiene	NS	NS	NS	NS
4-Chloro-3-methylphenol	56	59	50	46
Hexachlorocyclopentadiene	NS	NS	NS	NS
2,4,6-Trichlorophenol	NS	NS	NS	NS
2-Chloronaphthalene	NS	NS	NS	NS
Dimethyl phthalate	NS	NS	NS	NS
Acenaphthylene	NS	NS	NS	NS
Acenaphthene	57	103	54	53
2,4-Dinitrophenol	NS	NS	NS	NS
4-Nitrophenol	37	60	52	47
2,4-Dinitrotoluene	32	50	56	55
2,6-Dinitrotoluene	NS	NS	NS	NS
Diethyl phthalate	NS	NS	NS	NS
4-Chlorophenyl phenylether	NS	NS	NS	NS
Fluorene	NS	NS	NS	NS
4,6-Dinitro-2-methylphenol	NS	NS	NS	NS
N-Nitrosodiphenylamine	NS	NS	NS	NS
4-Bromophenyl phenylether	NS	NS	NS	NS
Hexachlorobenzene	NS	NS	NS	NS
Pentachlorophenol	44	50	34	33
Phenanthrene	NS	NS	NS	NS
Anthracene	NS	NS	NS	NS
Di-n-Butyl phthalate	45	71	52	47

(continued)

TABLE 8. (Continued)

	Soil No. 1 Spike	Soil No. 2 Dup Spike	Sludge No. 1 Spike	Sludge No. 2 Dup Spike
8270 Compounds	% Recov	% Recov	% Recov	% Recov
Fluoranthene	NS	NS	NS	NS
Pyrene	40	451	54	50
Butyl benzyl phthalate	NS	NS	NS	NS
3,3'-Dichlorobenzidine	NS	NS	NS	NS
Benzo(a)anthracene	NS	NS	NS	NS
Bis(2-ethylhexyl)phthalate	NS	NS	NS	NS
Chrysene	NS	NS	NS	NS
Di-n-octyl phthalate	NS	NS	NS	NS
Benzo(b)fluoranthene	NS	NS	NS	NS
Benzo(k)fluoranthene	NS	NS	NS	NS
Benzo(a)pyrene	NS	NS	NS	NS
Indeno(1,2,3-cd)pyrene	NS	NS	NS	NS
Dibenzo(a,h)anthracene	NS	NS	NS	NS
Benzo(g,h,i)perylene	NS	NS	NS	NS
Benzyl alcohol	NS	NS	NS	NS
2-Methyl phenol	NS	NS	NS	NS
4-Methyl phenol	NS	NS	NS	NS
Benzoic acid	NS	NS	NS	NS
4-Chloroaniline	NS	NS	NS	NS
2-Methylnaphthalene	NS	NS	NS	NS
2,4,5-Trichlorophenol	NS	NS	NS	NS
2-Nitroaniline	NS	NS	NS	NS
3-nitroaniline	NS	NS	NS	NS
Dibenzofuran	NS	NS	NS	NS
2,6 Dinitrotoluene	NS	NS	NS	NS
4-Nitroaniline	NS	NS	NS	NS
Date Analyzed	10/10/88	10/10/88	10/3/88	10/3/88
Date Extracted	10/4/88	10/4/88	10/3/88	10/3/88

Surrogates	Percent Recovery (%)			
2-Fluorophenol	45	45	69	58
Phenol-d_5	55	55	71	60
Nitrobenzene-d_5	75	75	79	72
2-Fluorobiphenyl	65	65	76	72
2,4,6-Tribromophenol	20	10	83	82
p-Terphenyl-d_{14}	65	75	84	80

TABLE 9. PESTICIDES AND PCBs MATRIX SPIKE RESULTS

	Soil No. 1 Spike	Soil No. 2 Dup Spike	Sludge No. 1 Spike	Sludge No. 2 Dup Spike
Pesticides and PCBs	% Recov	% Recov	% Recov	% Recov
Alpha BHC	NS	NS	NS	NS
Beta BHC	NS	NS	NS	NS
Gamma BHC	77	75	166	110
Delta BHC	NS	NS	NS	NS
Heptachlor	70	61	260	120
Aldrin	96	85	190	140
Heptachlor Epoxide	NS	NS	NS	NS
Endosulfan I	NS	NS	NS	NS
Dieldrin	120	110	380	160
4,4'-DDE	NS	NS	NS	NS
Endrin	160	150	480	150
Endosulfan II	NS	NS	NS	NS
4,4'-DDD	NS	NS	NS	NS
Endosulfan Sulfate	NS	NS	NS	NS
4'4'-DDT	58	71	240	89
Endrin Aldehyde	NS	NS	NS	NS
Endrin Ketone	NS	NS	NS	NS
Methoxychlor	NS	NS	NS	NS
Chlordane	NS	NS	NS	NS
Toxaphene	NS	NS	NS	NS
Aroclor-1016	NS	NS	NS	NS
Aroclor-1221	NS	NS	NS	NS
Aroclor-1232	NS	NS	NS	NS
Aroclor-1242	NS	NS	NS	NS
Aroclor-1248	NS	NS	NS	NS
Aroclor-1254	NS	NS	NS	NS
Aroclor-1260	NS	NS	NS	NS
Date Extracted:	10/4/88	10/4/88	10/3/88	10/3/88
Date Analyzed:	10/13/88	10/13/88	10/14/88	10/14/88

Surrogates	Percent Recoveries (%)			
DiButyl Chlorendate:	100	96	45	13

TABLE 10. METALS MATRIX SPIKE RESULTS

Pesticides and PCBs	EPA Method	Soil No. 1 Spike % Recov	Soil No. 2 Dup Spike % Recov	Sludge No. 1 Spike % Recov	Sludge No. 2 Dup Spike % Recov
Aluminum	6010	106	0.2	101	2.7
Antimony	7041	90	0	86	0.6
Arsenic	7060	78	1.5	81	3.0
Barium	6010	93	1.0	104	3.9
Beryllium	6010	89	4.1	96	1.7
Cadmium	6010	91	11	90	1.7
Calcium	6010	121	0.3	100	39
Chromium	6010	87	3.2	95	2.8
Cobalt	6010	84	2.0	96	0.8
Copper	6010	89	3.0	98	3.3
Iron	6010	75	0.5	79	12
Lead	6010	82	1.6	89	2.0
Magnesium	6010	84	1.6	95	0.7
Manganese	6010	80	1.5	99	4.1
Nickel	6010	87	1.5	92	2.8
Selenium	7740	74	2.5	113	13
Silver	6010	71	0	88	1.8
Sodium	6010	111	0.4	104	1.2
Thallium	7841	92	5.1	108	4.2
Vanadium	6010	89	1.8	98	1.2
Zinc	6010	95	12	96	2.9

TABLE 11. RESULTS FOR SPIKED SLUDGE NO. 1 LEACHATES

	Amount Found (µg/L)				Amount Spiked (µg/L)		% Recovery (a)				
Analyte	Native level	Spiked Set 1	Spiked Set 2	Spiked Set 3	Set 1	Set 2,3	Set 1	Set 2	Set 3	Avg (b)	%RSD (c)
Acetone	46.9	536	837	592	1,200	1,600	40.8	49.4	34.1	41.4	18.6%
Acrylonitrile	ND	53.5	569	541	600	800	8.92	71.1	67.6	49.2	71.0%
Benzene	1.08	186	317	344	600	800	30.8	39.4	42.8	37.7	16.4%
n-Butyl alcohol (1-Butanol)	ND	520	839	952	1,200	1,600	43.3	52.5	59.5	51.8	15.6%
Carbon disulfide	1.89	60.4	145	199	600	800	9.76	17.8	24.6	17.4	42.8%
Carbon tetrachloride	ND	90.7	202	253	600	800	15.1	25.3	31.6	24.0	34.6%
Chlorobenzene	ND	255	368	373	600	800	42.5	46.0	46.6	45.1	4.96%
Chloroform	0.548	250	396	436	600	800	41.6	49.4	54.4	48.5	13.3%
1,2-Dichloroethane	ND	328	505	536	600	800	54.6	63.1	67.0	61.6	10.3%
1,1-Dichloroethene	ND	88.5	182	234	600	800	14.7	22.8	29.3	22.3	32.7%
Ethyl acetate	ND	795	1,153	1,262	1,200	1,600	66.3	72.1	78.8	72.4	8.70%
Ethylbenzene	1.22	169	270	286	600	800	27.9	33.6	35.6	32.4	12.3%
Ethyl ether	0.613	581	715	732	1,200	1,600	48.3	44.6	45.7	46.2	4.11%
Isobutanol (4-Methyl-1-propanol)	ND	ND	ND	ND	1,200	1,600	0.0	0.0	0.0	0.0	N/A%
Methylene chloride	1.04	202	211	227	600	800	33.4	26.3	28.3	29.3	12.6%
Methyl ethyl ketone (2-Butanone)	26.6	653	1,028	982	1,200	1,600	52.2	62.6	59.7	58.2	9.22%
Methyl isobutyl ketone	1.66	894	1,200	1,305	1,200	1,600	74.3	74.9	81.4	76.9	5.13%
1,1,1,2-Tetrachloroethane	0.899	274	415	437	600	800	45.4	51.8	54.5	50.6	9.19%
1,1,2,2-Tetrachloroethane	1.53	401	491	605	600	800	66.6	61.2	75.4	67.7	10.6%
Tetrachloroethene	0.745	105	199	216	600	800	17.4	24.8	26.9	23.0	21.6%
Toluene	1.88	222	360	375	600	800	36.7	44.8	46.7	42.7	12.4%
1,1,1-Trichloroethane	ND	141	281	334	600	800	23.5	35.2	41.7	33.5	27.6%
1,1,2-Trichloroethane	ND	362	513	532	600	800	60.3	64.1	66.6	63.7	4.92%
Trichloroethene	1.38	196	355	366	600	800	32.5	44.2	45.6	40.8	17.7%
Trichlorofluoromethane	0.368	39.8	88.7	148	600	800	6.57	11.0	18.4	12.0	49.8%
1,1,2-Trichloro-trifluorethane	ND	20.7	55.0	85.9	600	800	3.44	6.88	10.7	7.02	52.0%
Vinyl chloride	ND	33.7	68.4	117	600	740	5.62	9.24	15.8	10.2	50.7%
o- and p-Xylene (d)	2.75	371	567	596	1,200	1,600	30.7	35.3	37.1	34.4	9.60%

(a) % Recovery = (amount found in spiked set - amount found at native level) / amount spiked * 1

(b) Avg = average of the three sets % recovery

(c) %RSD = (Standard deviation/Avg of values) * 100

(d) o- and p-Xylene coelute under the GC conditions specified in Method 8240.

(e) Quantitation limits
- Native level determination: 20 to 200 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 40 to 400 µg/L.
- Spiked matrix determination: 100 to 1,000 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 400 to 4,000 µg/L.

TABLE 12. RESULTS FOR SPIKED SLUDGE NO. 2 LEACHATES

	Amount Found (µg/L)				Amount Spiked (µg/L)		% Recovery (a)				
Analyte	Native level	Spiked Set 1	Spiked Set 2	Spiked Set 3	Set 1	Set 2,3	Set 1	Set 2	Set 3	Avg (b)	%RSD (c)
Acetone	44.2	587	641	615	1,200	1,600	45.3	37.3	35.7	39.4	13.0%
Acrylonitrile	ND	62.1	639	589	600	800	10.4	79.8	73.7	54.6	70.4%
Benzene	0.887	235	349	328	600	800	39.0	43.5	40.9	41.2	5.46%
n-Butyl alcohol (1-Butanol)	ND	643	995	935	1,200	1,600	53.6	62.2	58.4	58.1	7.41%
Carbon disulfide	1.85	120	200	202	600	800	19.8	24.8	25.0	23.2	12.8%
Carbon tetrachloride	ND	180	244	254	600	800	30.0	30.5	31.8	30.7	3.03%
Chlorobenzene	ND	312	422	397	600	800	51.9	52.8	49.6	51.4	3.22%
Chloroform	0.318	295	439	415	600	800	49.0	54.8	51.8	51.9	5.53%
1,2-Dichloroethane	ND	367	559	526	600	800	61.1	69.9	65.7	65.6	6.73%
1,1-Dichloroethene	ND	151	217	219	600	800	25.1	27.1	27.3	26.5	4.67%
Ethyl acetate	ND	879	1,302	1,212	1,200	1,600	73.2	81.4	75.7	76.8	5.46%
Ethylbenzene	0.824	242	320	320	600	800	40.2	39.9	39.8	40.0	0.555%
Ethyl ether	1.37	544	774	680	1,200	1,600	45.2	48.3	42.4	45.3	6.55%
Isobutanol (4-Methyl-1-propanol)	ND	ND	ND	ND	1,200	1,600	0.0	0.0	0.0	0.0	N/A%
Methylene chloride	1.03	147	241	220	600	800	24.3	29.9	27.4	27.2	10.5%
Methyl ethyl ketone (2-Butanone)	14.8	662	960	868	1,200	1,600	53.9	59.1	53.4	55.5	5.70%
Methyl isobutyl ketone	2.07	930	1,319	1,257	1,200	1,600	77.3	82.3	78.5	79.4	3.32%
1,1,1,2-Tetrachloroethane	0.515	327	471	448	600	800	54.4	58.8	55.9	56.4	3.93%
1,1,2,2-Tetrachloroethane	1.16	426	611	588	600	800	70.8	76.2	73.3	73.4	3.71%
Tetrachloroethene	1.07	180	236	247	600	800	29.8	29.4	30.7	30.0	2.32%
Toluene	1.31	284	399	375	600	800	47.1	49.7	46.8	47.9	3.42%
1,1,1-Trichloroethane	ND	224	311	312	600	800	37.3	38.8	39.0	38.4	2.43%
1,1,2-Trichloroethane	ND	391	574	532	600	800	65.1	71.8	66.5	67.8	5.15%
Trichloroethene	1.23	267	388	362	600	800	44.3	48.4	45.1	45.9	4.69%
Trichlorofluoromethane	0.383	100	113	122	600	800	16.6	14.0	15.2	15.3	8.28%
1,1,2-Trichloro-trifluorethane	ND	64.6	68.7	74.0	600	800	10.8	8.58	9.25	9.53	11.8%
Vinyl chloride	ND	75.4	102	106	600	740	12.6	13.8	14.4	13.6	6.83%
o- and p-Xylene (d)	1.73	516	687	664	1,200	1,600	42.9	42.8	41.4	42.4	1.99%

(a) % Recovery = (amount found in spiked set - amount found at native level) / amount spiked * 1

(b) Avg = average of the three sets % recovery

(c) %RSD = (Standard deviation/Avg of values) * 100

(d) o- and p-Xylene coelute under the GC conditions specified in Method 8240.

(e) Quantitation limits

- Native level determination: 20 to 200 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 40 to 400 µg/L.
- Spiked matrix determination: 100 to 1,000 µg/L, except acetone, 1-butanol, ethyl acetate, ethyl ether, isobutanol, 2-butanone, methyl isobutyl ketone, and o- and p-xylene, which are 400 to 4,000 µg/L.

APPENDIX C

METHOD 1312

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic contaminants present in samples of soils, wastes, and wastewaters.

1.2 If a total analysis of the soil, waste, or wastewater demonstrates that individual contaminants are not present, or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, Method 1312 need not be run.

1.3 If an analysis of any one of the liquid fractions of the 1312 extract indicates that a regulated compound is present at such high levels that even after accounting for dilution from the other fractions of the extract the concentration would be above the regulatory threshold for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile contaminant exceeds the regulatory threshold for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory threshold, because recovery of volatiles using the bottle extractor is usually low.

2.0 SUMMARY OF METHOD (See Figure 1)

2.1 For samples containing less than 0.5 percent solids, the sample, after filtration through a 0.6 - 0.8 µm glass fiber filter, is defined as the extract. For samples containing greater than 0.5 percent solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid phase of the separated sample is reduced (if necessary) and is extracted with an amount of extraction fluid equal to 20 times the weight of the sample. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatiles. Following extraction, the liquid extract is separated from the sample by 0.6 - 0.8 µm glass fiber filter.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation Apparatus - an acceptable agitation apparatus is one which is capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm (see Figure 1). Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessel - acceptable extraction vessels are those that are listed below.

4.2.1 Zero Headspace Extraction Vessel (ZHE) - This device is for use only when the soil is being tested for the mobility of volatile constituents (see Table 1). The ZHE is an extraction vessel that allows for liquid/solid separation within the device and which effectively precludes headspace (as depicted in Figure 3). This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500 to 600 mL and be equipped to accommodate a 90-mm filter. Suitable ZHE devices known to EPA are identified in Table 3. These devices contain viton O-rings which should be replaced frequently. For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted. The ZHE should be checked after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

4.2.2 Bottle Extraction Vessel - When the soil is being evaluated for other than volatile contaminants, an extraction vessel that does not preclude headspace (e.g., a 2-liter bottle) is used. Suitable extraction vessels include bottles made from various materials, depending on the contaminants to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used over other types of glass, especially when inorganics are of concern. Plastic bottles may be used only if inorganics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.2.3 Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.4) refers to pounds-per-square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.3 Filtration Devices - It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (see Figure 3) - When the waste is being evaluated for volatiles, the zero-headspace extraction vessel is used for filtration. The device shall be capable of supporting and keeping in place the fiber filter, and be able to withstand the pressure needed to accomplish separation (50 psi).

> NOTE: When is it suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder - When the soil is being evaluated for other than volatile compounds, a filter holder capable of supporting a glass fiber filter and able to withstand 50 psi or more of pressure shall be used. These devices shall have a minimum internal volume of 300 mL and be equipped to accomodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 liters or greater are recommended).

4.3.3 Materials of Construction - Filtration devices shall be made of inert materials which will not leach or absorb soil components. Glass, polytetrafluoroethylene (PTFE) or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene, or polyvinyl chloride may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are constituents of concern.

4.4 Filters - Filters shall be made of borosilicate glass fiber, shall have an effective pore size of 0.6 - 0.8 µm and shall contain no binder materials. Filters known to EPA to meet these requirements are identified in Table 5. When evaluating the mobility of metals, filters should be acid-washed prior to use by rinsing with 1.0N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 liter per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters - Any of the commmonly available pH meters are acceptable.

4.6 ZHE Extract Collection Devices - TEDLAR® bags, glass, stainless steel or PTFE gas tight syringes are used to collect the initial liquid phase and the final phase when using the ZHE device. These devices are recommended for the following condition.

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 percent of total waste), the TEDLAR® bag should be used to collect and combine the initial liquid and solid extract. The syringe is not recommended in these cases.

4.6.2 If a waste contains a significant amount of nonaqueous initial liquid phase (i.e., >1 percent of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use on or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant solid phase (is 100 percent liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices - any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is recommended.

4.8 Laboratory Balance - any laboratory balance accurate to within ± 0.01 g may be used (all weight measurements are to be within ± 0.1 g).

5.0 REAGENTS

5.1 Reagent Water - reagent water is defined as water in which an interferent is not observed at or above the method detection limit of the analyte(s) of interest. For non-volatile extractions, ASTM Type II water, or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.1.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb 300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.1.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5° C, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle under zero headspace and seal with a Teflon lined septum and cap.

5.2 Sulfuric Acid/Nitric Acid (60/40 weight percent mixture) H_2SO_4/HNO_3 - Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

5.3 Extraction Fluids -

5.3.1 Extraction Fluid No. 1 - This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River.

5.3.2 Extraction Fluid No. 2 - This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.3.3 Extraction Fluid No. 3 - This fluid is reagent water (ASTM Type II water, or equivalent) used to determine cyanide and volatiles leachability.

NOTE: It is suggested that these extxraction fluids be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately.

5.4 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 At least three separate representative samples should be collected. The first sample is used to determine if particle-size reduction is necessary for solid samples, and is used to determine the percent solids for a liquid or multi-phasic sample. The second sample is used for the extraction of non-volatiles and the third sample is used for the extraction of volatiles.

6.3 Preservatives shall not be added to samples.

6.4 Samples shall be refrigerated to minimize loss of volatile organics and to retard biological activity.

6.5 When the soil is to be evaluated for volatile contaminants, care should be taken to minimize the loss of volatiles. Samples shall be taken and stored in a manner to prevent the loss of volatile contaminants. If possible, it is recommended that any necessary particle-size reduction be conducted as the sample is being taken.

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. If they need to be stored, even for a short period of time, storage shall be at 4° C, and samples for volatiles analysis shall not be allowed to come into contact with the atmosphere (i.e., no headspace). See Section 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 The preliminary 1312 evaluations are performed on a minimum 100 g representative sample of solid sample that will not actually undergo 1312 extraction (designated as the first sample in Step 6.2).

Percent Solids Determination

7.2 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., 100 percent solid), weigh out a representative subsample (100 gram minimum) and proceed to Step 7.5.

7.3 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device discussed in Step 4.3, and is outlined in Steps 7.3.1 to 7.3.6.

7.3.1 Pre-weigh the filter and the container which will receive the filtrate. Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

7.3.2 Weigh out a representative subsample (100 g minimum) and record weight.

7.3.3 Allows slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration.

7.3.4 Transfer the waste sample to the filter holder.

NOTE: If the sample material has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.2 to determine the weight of the sample which will be filtered.

Gradually apply vacuum or gentle pressure of 1 - 10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.5 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.3.4, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carred through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.3.6 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.3.1) from the total weight of the filtrate-filled container. The weight of the solid phase of the sample is determined by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.3.2 or 7.3.4. Record the weight of the liquid and solid phases.

$$\%\ \text{solids} = \frac{\text{weight of solid (Step 7.3.6)}}{\text{total weight of waste (Step 7.3.2 or 7.3.4)}} \times 100$$

NOTE: If the weight of the solid phase of the waste is less than 75 grams, obtain a new sample and repeat the procedure.

7.4 The sample will be handled differently from this point, depending on whether it contains more or less than 0.5 percent solids. If the filtered sample obviously has greater than 0.5 percent solids go to Step 7.5. If it appears that the solid may comprise less than 0.5 percent of the total waste, the percent solids will be determined as follows.

7.4.1 Remove the solid phase and filter from the filtration apparatus.

7.4.2 Dry the filter and solid phase at 100 ± 20° C until two successive weighings yield the same value. Record final weight.

7.4.3 Calculate the percent dry solids as follows:

$$\%\ \text{dry solids} = \frac{(\text{wt. of dry waste + filter}) - \text{tared wt. of filter}}{\text{initial wt. of waste (Step 7.3.2 or 7.3.4)}}$$

7.4.4 If the solid comprises less than 0.5 percent of the sample, the solid is discarded and the liquid phase is defined as the extract. Proceed to Step 7.6.

7.4.5 If the solid is greater than or equal to 0.5 percent of the sample, return to Step 7.3, and begin the procedure with a new sample. Do not extract the solid that has been dried.

Particle-Size Reduction

7.5 Determine whether the sample requires particle-size reduction. If the sample passes through a 9.5 mm (3/8-inch) standard sieve, particle-size reduction is not required (proceed to Step 7.6). If portions of the sample do not pass through the sieve, then the oversize portion of the sample will have to be prepared for extraction by crushing, cutting, or grinding to a surface area or particle-size that passes a 9.5 mm sieve.

Extraction for Non-volatiles

7.6 If volatiles are involved, proceed to Step 7.7. If the sample is 100 percent solid, proceed to Step 7.6.3.5. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. However, a minimum sample size of 100 grams shall be used. If the amount of extract generated by a single 1312 extract will not be sufficient to perform all of the analyses, it is recommended that more than one extraction be performed and the extracts be combined and then aliquoted for analysis.

7.6.1 Weigh out a representative subsample of the sample (designated as the second sample in Step 6.2) and transfer to the filter holder extractor vessel.

7.6.2 Determine the appropriate extraction fluid to use:

For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid No. 1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid No. 2 should be used.

For waste and wastewater, extraction fluid No. 1 should be used.

For cyanide-containing wastes and/or soils, extraction fluid No. 3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.6.3 If the waste contains <0.5 percent dry solids (Step 7.4.3), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For waste containing >0.5 percent dry solids (Step 7.4.3), use the percent solids information obtained in Step 7.4.3 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.6.3.1 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.6.3.2 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4° C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before fitering.

> NOTE: If waste material (>1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.6.1, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1 - 10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.6.3.3 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the liquid phase. The liquid phase may now be either analyzed (see Steps 7.6.7 - 7.7.9) or stored at 4° C until time of extract analysis.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.6.3.2, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.6.3.4 If the waste contains <0.5 percent dry solids (see Step 7.4.3), the filtrate is defined as the 1312 extract. Proceed to Step 7.6.7. If the waste contains >0.5 percent dry solids (see Step 7.4.3), and if particle-size reduction of the solid was needed in Step 7.5, proceed to Step 7.6.3.5. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.6.4.

7.6.3.5 Prepare the solid portion of the waste for extraction as described in Step 7.5. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase (if the initial phase was not 100 percent solid).

> NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.6.4 Determine the amount of extraction fluid to add based on the following formula:

$$\text{wt. of extraction fluid (mL)} = \frac{20 \times \%\ \text{solids (Step 7.2 or 7.3.6)} \times \text{wt. of waste filtered (Step 7.2 or 7.6.3.3)}}{100}$$

Slowly add the amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction is to take place) shall be maintained at 22 ± 3° C during the extraction period.

> NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.6.5 Following the 18 ± 2 hour extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a glass fiber filter.

7.6.6 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 7.6.5 is defined as the extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 7.6.5 and the initial liquid phase (Step 7.6.3.3) are collectively defined as the extract.

> NOTE: The initial liquid phase and the filtered liquid material can be combined and analyzed if they are miscible. The phases must be analyzed separately (see Step 7.6.8) if they are not miscible. If the filtered liquid material is multiphasic, do not combine the phases for analysis, but analyze them separately and mathematically combine the results.

7.6.7 Following collection of the 1312 extract it is recommended that the pH of the extract be recorded. The extract should be immediately aliquoted for analysis and properly preserved (metals aliquots must be acidified with nitric acid to pH <2; all other aliquots must be stored under refrigeration (4° C) until analyzed). The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals, other than mercury, shall be acid digested.

7.6.8 If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (1)

C_1 = The concentration of the contaminant of concern in the first phase (mg/L)

V_2 = The volume of the second phase (1)

C_2 = The concentration of the contaminant of concern in the second phase (mg/L)

7.6.9 Compare the contaminant concentrations in the 1312 extract with the appropriate regulatory thresholds. Refer to Section 8.0 for quality assurance requirements.

Extraction for Volatiles

7.7 Procedure When Volatiles are Involved -

7.7.1 The ZHE device is used to obtain 1312 extracts for volatile analysis only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.). The ZHE device has approximately a 500 mL internal capacity. Although a minimum sample size of 100 g was required in the Step 7.2 procedure, the ZHE can only accommodate a maximum of 25 g of solid, due to the need to add an amount of extraction fluid equal to 20 times the weight of the soil. The ZHE is charged with sample only once and the device is not opened until the final extract has been collected. Although the following procedure allows for particle-size reduction during the conduct of the procedure, this could result in the loss of volatile compounds. If possible, particle-size reduction (see Step 7.5) should be conducted on the sample as it is being taken (e.g., particle-size may be reduced by crumbling). If necessary particle-size reduction may be conducted during the procedure. In carrying out the following steps, do not allow the soil to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4° C) to minimize the loss of volatiles. Pre-weigh the evaculated container which will receive the filtrate (see Step 4.6), and set aside. If using a TEDLAR® bag, all air must be expressed from the device.

7.7.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid).

7.7.3 If the waste is 100 percent solid, weigh out a representative subsample (25 g maximum) of the waste, record weight, and proceed to Step 7.7.5.

7.7.4 If the waste contains <0.5 percent dry solids (Step 7.4.3), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of volatile analyses required. For wastes containing >0.5 percent dry solids (Step 7.4.3), use the percent solids information obtained in Step 7.4.3 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows.

7.7.4.1 For wastes containing <5 percent solids (see Step 7.3.6), weigh out a representative 500 g sample of waste and record the weight. Proceed to Step 7.7.5.

7.7.4.2 For wastes containing >5 percent solids (see Step 7.3.6), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\%\text{ solids (Step 7.3.6)}} \times 100$$

Weigh out a representative subsample of the waste of the appropriate size and record the weight.

7.7.5 If particle-size reduction of the solid portion of the waste was required in Step 7.5, proceed to Step 7.7.6. If particle-size reduction was not required in Step 7.5, proceed to Step 7.7.7.

7.7.6 Prepare the waste for extraction as described in Step 7.5. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4° C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.7.7.

7.7.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.7.8 Quantitatively transfer the amount of the sample determined in Steps 7.7.4.1 or 7.7.4.2 to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate. Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1 - 10 psi to a maximum of 50 psi to force most of the headspace out of the device.

7.7.9 Attached the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1 - 10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.7.10 The material in the ZHE is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 percent dry solids (see Step 7.4.3), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.7.18.

7.7.11 The liquid phase may now be either analyzed immediately (see Steps 7.7.18 and 7.7.19) or stored at 4° C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid No. 3 to add to the ZHE as follows:

$$\text{wt. of extraction fluid} = \frac{\begin{array}{c}20 \times \%\ \text{solids (Steps 7.2 or 7.3.6) x wt. of} \\ \text{waste filtered (Steps 7.6.3.3 or 7.7.3)}\end{array}}{100}$$

7.7.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid No. 3 is used in all cases (see Step 5.3.3).

7.7.13 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.7.14 After the extraction fluid has been added, immediately close the inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Physically rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Put 5 to 10 psi behind the piston (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Repressurize the ZHE with 5 to 10 psi and check all ZHE fittings to ensure that they are closed.

7.7.15 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate the ZHE at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of the room in which extraction is to occur) shall be maintained at 22 ± 3° C during agitation.

7.7.16 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking, and the procedure must be repeated with a new sample. If the pressure within the device has been maintained, the material in the extractor vessel is separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phaes, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.7.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.7.17 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 7.7.16 is defined as the extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 7.7.16 and the initial liquid phase (Step 7.7.11) are collectively defined as the extract.

> NOTE: The initial liquid phase and the filtered liquid material can be combined and analyzed if they are miscible. The phases must be analyzed separately (see Step 7.6.8) if they are not miscible. If the filtered liquid material is multiphasic, do not combine the phases for analysis, but analyze them separately and mathematically combine the results.

7.7.18 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4° C until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (1)
C_1 = The concentration of the contaminant of concern in the first phase (mg/L)
V_2 = The volume of the second phase (1)
C_2 = The concentration of the contaminant of concern in the second phase (mg/L)

7.7.19 Compare the contaminant concentrations in the 1312 extract with the appropriate regulatory thresholds. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 All data, including quality assurance data, should be maintained and available for reference or inspection.

8.2 A minimum of 1 blank (extraction fluid No. 1) for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment are occurring.

8.3 For each analytical batch (up to 20 samples), it is recommended that a matrix spike be performed. Addition of matrix spikes should occur once the

1312 extract has been generated (i.e., should not occur prior to performance of the 1312 procedure). The purpose of the matrix spike is to monitor the adequacy of the analytical methods used on the 1312 extract and for determining if matrix interferences exist in analyte detection.

8.4 All quality control measures described in the appropriate analytical methods shall be followed.

8.5 The method of standard addition shall be employed for each analyte if: 1) recovery of the compound from the 1312 extract is not between 50 and 150 percent, or 2) if the concentration of the constituent measured in the extract is within 20 percent of the appropriate regulatory threshold. If more than one extraction is being run on samples of the same waste (up to 20 samples), the method of standard addition need be applied only once and the percent recoveries applied on the remainder of the extractions.

8.6 Samples must undergo 1312 extraction within the following time period after sample receipt: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days. 1312 extracts shall be analyzed after generation and preservation within the following periods: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals. An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentrations of contaminants leached from the soils were consistently reproducible, as shown by the low relative standard deviations (RSDs) of the recoveries (generally less than 10 percent for most of the compounds).

9.2 Precision results for volatiles. Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

10.1 Environmental Monitoring Systems Laboratory, "QA Support for RCRA Testing: Annual Report". EPA Contract 68-03-3249, January 1989.

Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

TABLE 1. VOLATILE CONTAMINANTS[1]

Compounds	CAS No.
Acetone	67-64-1
Acetonitrile	75-05-8
Acrolein	107-02-8
Acrylamide	79-06-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromomethane	74-83-9
Carbon disulfide	75-15-0
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroform	67-66-3
Chloromethane	74-87-3
p-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
cis-1,2-Dichloroethylene	156-59-2
Dichloromethane	75-09-2
1,2-Dichloropropane	78-87-5
1,3-Dichloropropene	542-75-6
Ethyl benzene	100-41-4
Isobutyl alcohol	78-83-1
Methyl ether ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Tetrachloromethane	56-23-5
Toluene	108-88-3
Tribromomethane (Bromoform)	75-25-2
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-7
Xylene	1330-20-7

[1] If any of these compounds are of concern, the zero-headspace extractor vessel shall be used. If other (non-volatile) compounds are of concern, the conventional bottle extractor shall be used.

TABLE 2. SUITABLE ROTARY AGITATION APPARATUS[1]

Company	Location	Model
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	4-vessel device, 6-vessel device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	4-vessel device, 6-vessel device
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	16-vessel device
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel device 5-vessel device
Millipore Corp.	Bedford, MA (800) 225-3384	4-vessel ZHE device or 4-one liter bottle extractor device
REXNORD	Milwaukee, WI (414) 643-2850	6-vessel device

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

TABLE 3. SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA, (215) 343-4490	C102., Mechanical Pressure Device
Associated Design and Manufacturing Co.	Alexandria, VA (703) 549-5999	3740-ZHB, Gas Pressure Device
Lars Lande Mfg.	Whitmore Lake, MI (313) 449-4116	Gas Pressure Device
Millipore Corp.	Bedford, MA, (800) 225-3384	SD1 P581 C5, Gas Pressure Device

[1] Any device that meets the specifications in Section 4.2.1 of the method is suitable.

TABLE 4. SUITABLE ZHE FILTER HOLDERS[1]

Company	Location	Model	Size
Micro Filtration Systems	Dublin, CA (415) 828-6010	302400	142 mm
Millipore Corp.	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm
Nucleopore Corp.	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the soil is suitable, providing that it is chemically compatible with the soil and the constitutents to be analyzed. Plastic devices (not listed above) may be used when only inorganic contaminants are of concern. The 142 mm size filter holder is recommended.

TABLE 5. -- SUITABLE FILTER MEDIA[1]

Company	Location	Model	Size[1]
Millipore Corp.	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corp.	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

TABLE 6. METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

	Eastern Soil (pH 4.2)			Western Soil (pH 5.0)	
	Amount Spiked (µg)	Amount Recovered* (µg)	%RSD	Amount Recovered* (µg)	%RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma-BHC (Lindane)	7440	230	16.3	1240	55.2
beta-BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

*Triplicate analyses.

**Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7. METHOD 1312 PRECISION RESULTS FOR VOLATILES

	Soil No. 1		Soil No. 2		Soil No. 3		Soil No. 4	
	(Western)		(Eastern)		(Western and Sludge)		(Western and Sludge)	
Compound Name	Avg. %Rec.*	%RSD	Avg. %Rec.*	%RSD	Avg. %Rec.**	%RSD	Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl-1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

*Triplicate analyses
**Six replicate analyses
***Five replicate analyses

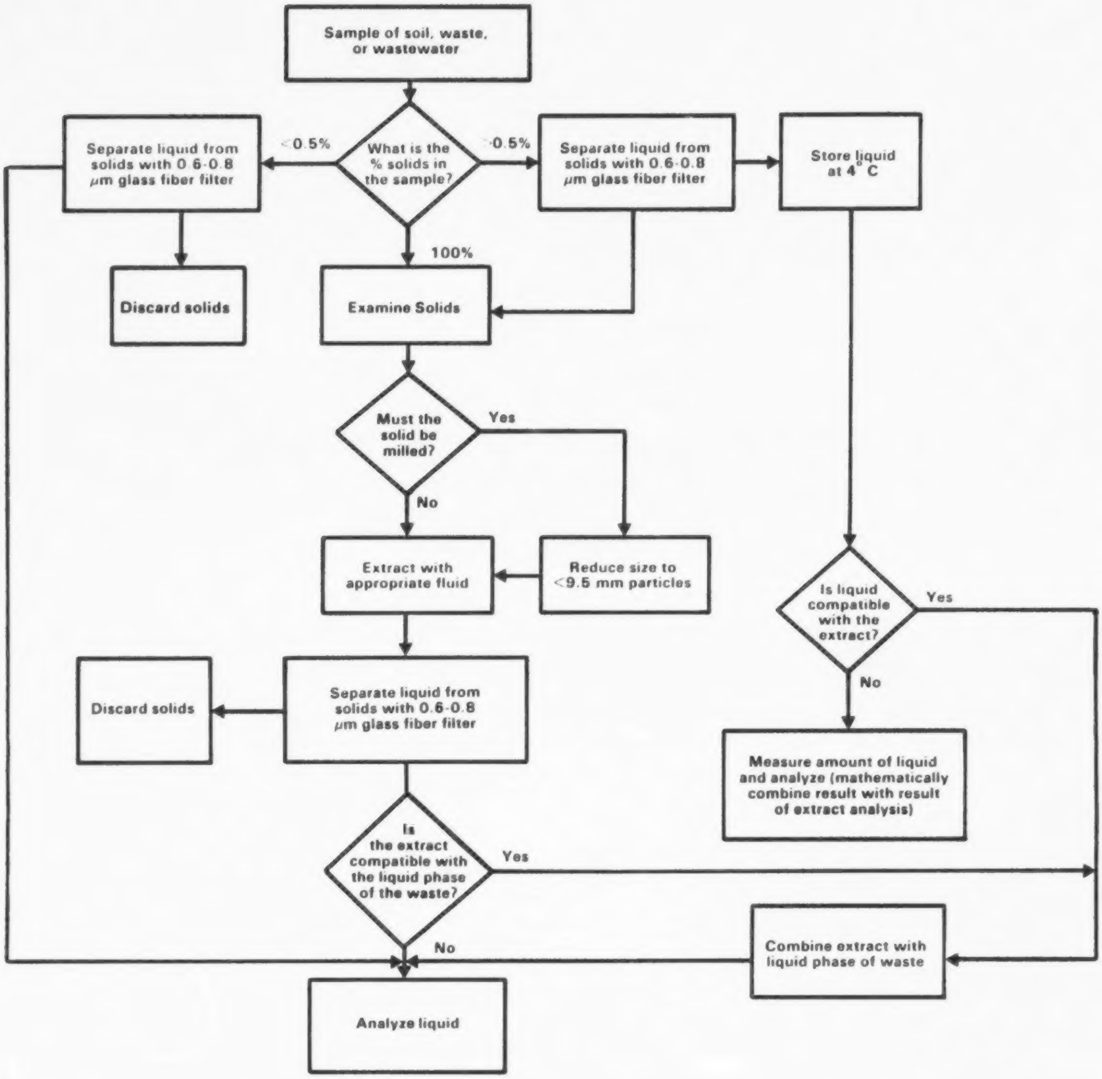

Sample of soil, waste, or wastewater
What is the % solids in the sample?
<0.5%
>0.5%
100%
Separate liquid from solids with 0.6-0.8 μm glass fiber filter
Separate liquid from solids with 0.6-0.8 μm glass fiber filter
Store liquid at 4° C
Discard solids
Examine Solids
Must the solid be milled?
Yes
No
Extract with appropriate fluid
Reduce size to <9.5 mm particles
Is liquid compatible with the extract?
Yes
No
Discard solids
Separate liquid from solids with 0.6-0.8 μm glass fiber filter
Measure amount of liquid and analyze (mathematically combine result with result of extract analysis)
Is the extract compatible with the liquid phase of the waste?
Yes
No
Combine extract with liquid phase of waste
Analyze liquid

Figure 1. Method 1312 flowchart.

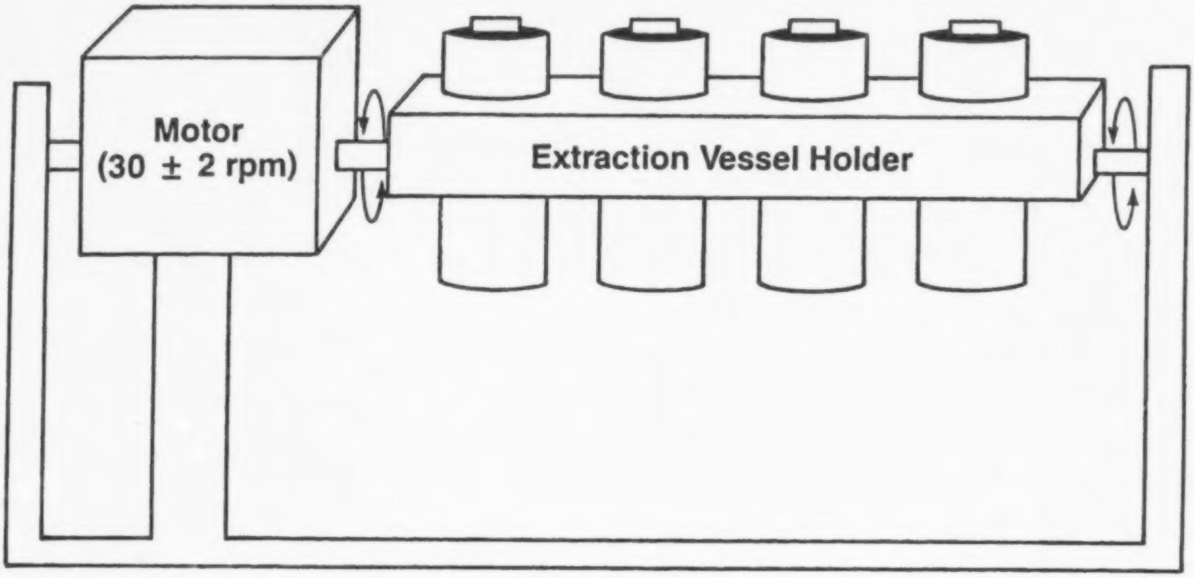

Motor
(30 ± 2 rpm)
Extraction Vessel Holder

Figure 2. Rotary agitation.

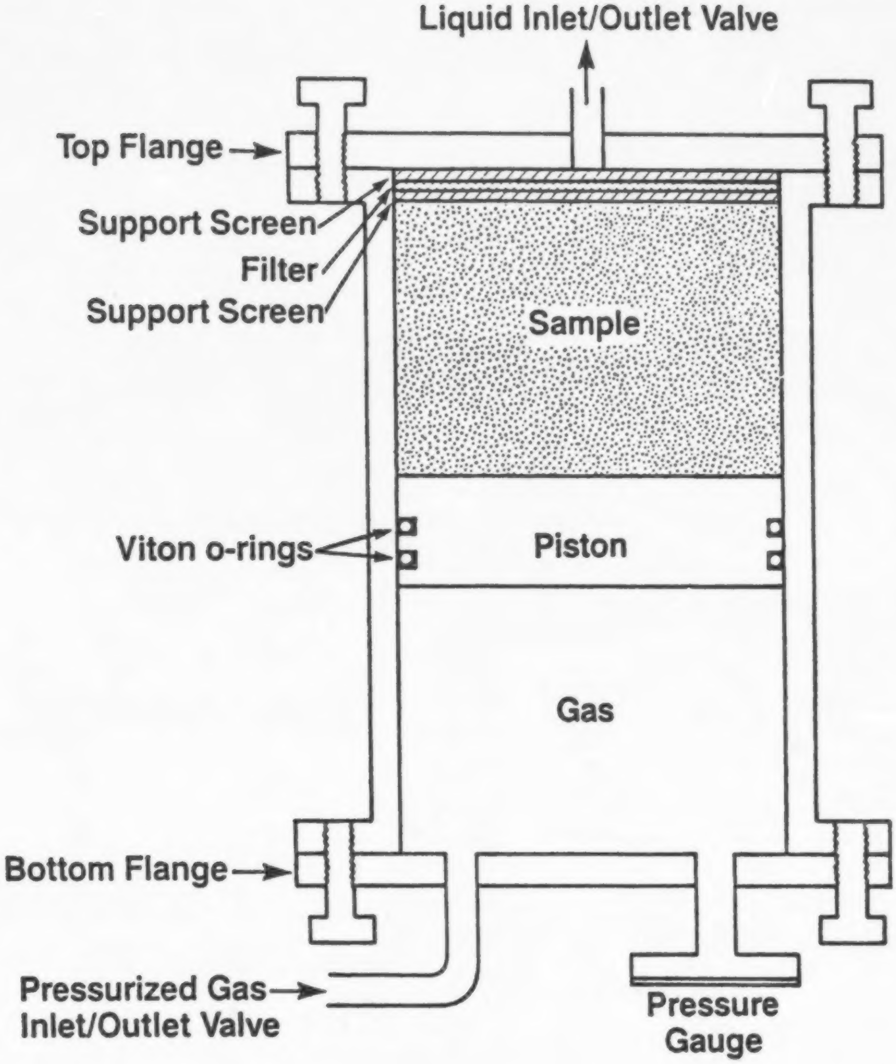

Liquid Inlet/Outlet Valve
Top Flange
Support Screen
Filter
Support Screen
Sample
Viton o-rings
Piston
Gas
Bottom Flange
Pressurized Gas Inlet/Outlet Valve
Pressure Gauge

Figure 3. Zero-headspace extractor (ZHE).

APPENDIX D

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

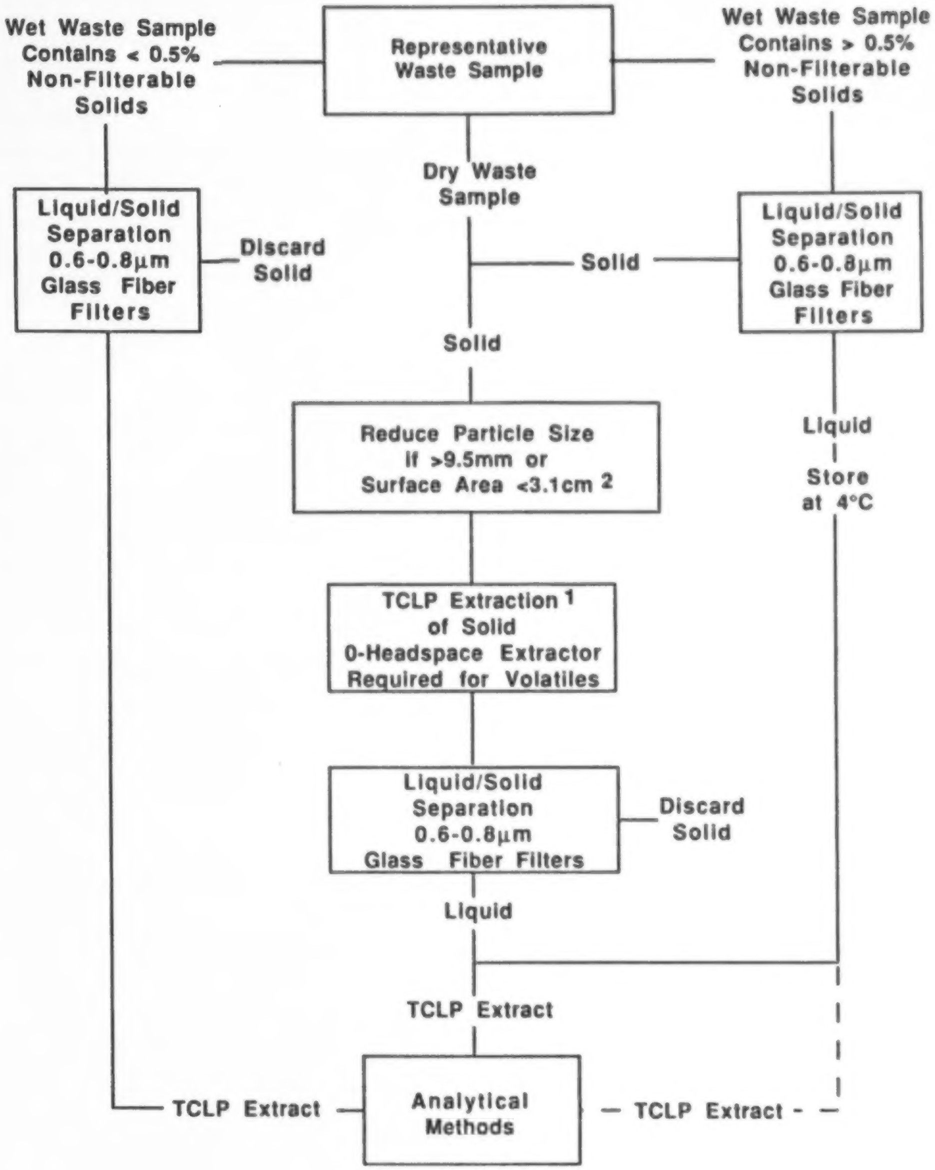
1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high levels that even after accounting for dilution from the other fractions of the extract the concentration would be above the regulatory threshold for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile contaminant exceeds the regulatory threshold for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory threshold, because recovery of volatiles using the bottle extractor is usually low.

2.0 SUMMARY OF METHOD (See Figure 1)

2.1 For liquid wastes (i.e., those containing less than 0.5 percent dry solid material), the waste, after filtration through a 0.6- to 0.8-μm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5 percent dry solid material, the particle-size of the waste is reduced (if necessary), and the liquid phase, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile contaminants (See Table 1 for a list of volatile compounds). Following extraction, the liquid


Wet Waste Sample Contains < 0.5% Non-Filterable Solids
Representative Waste Sample
Wet Waste Sample Contains > 0.5% Non-Filterable Solids
Liquid/Solid Separation 0.6-0.8μm Glass Fiber Filters
Discard Solid
Dry Waste Sample
Solid
Liquid/Solid Separation 0.6-0.8μm Glass Fiber Filters
Solid
Reduce Particle Size if >9.5mm or Surface Area <3.1cm 2
Liquid
Store at 4°C
TCLP Extraction 1 of Solid 0-Headspace Extractor Required for Volatiles
Liquid/Solid Separation 0.6-0.8μm Glass Fiber Filters
Discard Solid
Liquid
TCLP Extract
TCLP Extract
Analytical Methods
TCLP Extract

[1] The extraction fluid employed is a function of the alkakinity of the solid phase of the waste.

Figure 1. TCLP flowchart.

TABLE 1. VOLATILE CONTAMINANTS[1]

Compound	CAS No.
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
n-Butyl alcohol	71-36-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-8
1,1,2-Trichloroethane	79-00-5
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] If any or all of these compounds are of concern, the zero-headspace extractor vessel shall be used. If other (non-volatile) compounds are of concern, the conventional bottle extractor shall be used.

extract is separated from the solid phase by filtration through a 0.6- to 0.8-μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation Apparatus - The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (See Figure 2) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessel -

4.2.1 Zero-Headspace Extraction Vessel (ZHE) - This device is for use only when the waste is being tested for the mobility of volatile constituents (i.e., those listed in Table 1). The ZHE (depicted in Figure 3) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (See step 4.3.1). The vessels shall have an internal volume of 500- to 600-mL and be equipped to accommodate a 90-mm filter. The devices contain Viton O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

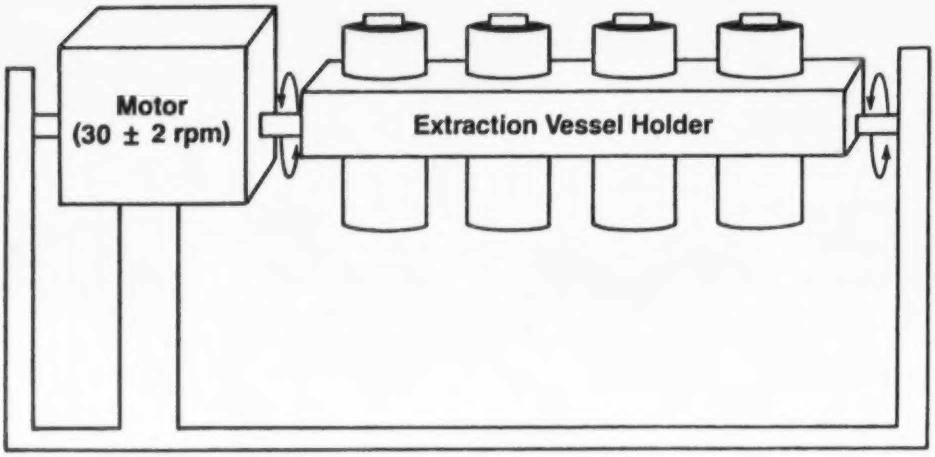


Figure 2. Rotary agitation apparatus.

TABLE 2. SUITABLE ROTARY AGITATION APPARATUS[1]

Company	Location	Model
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-ZHE device or 8-bottle extractor device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	4-vessel device, 6-vessel device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel device 4-vessel device
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	16-vessel device
Lars Lande Manufacturing	Whitmore Lake, MI (313)449-4116	10-vessel device, 5-vessel device
Millipore Corp.	Bedford, MA (800) 225-3384	4-vessel ZHE device or 4-bottle extractor device
REXNORD	Milwaukee, WI (414) 643-2850	6-vessel device

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

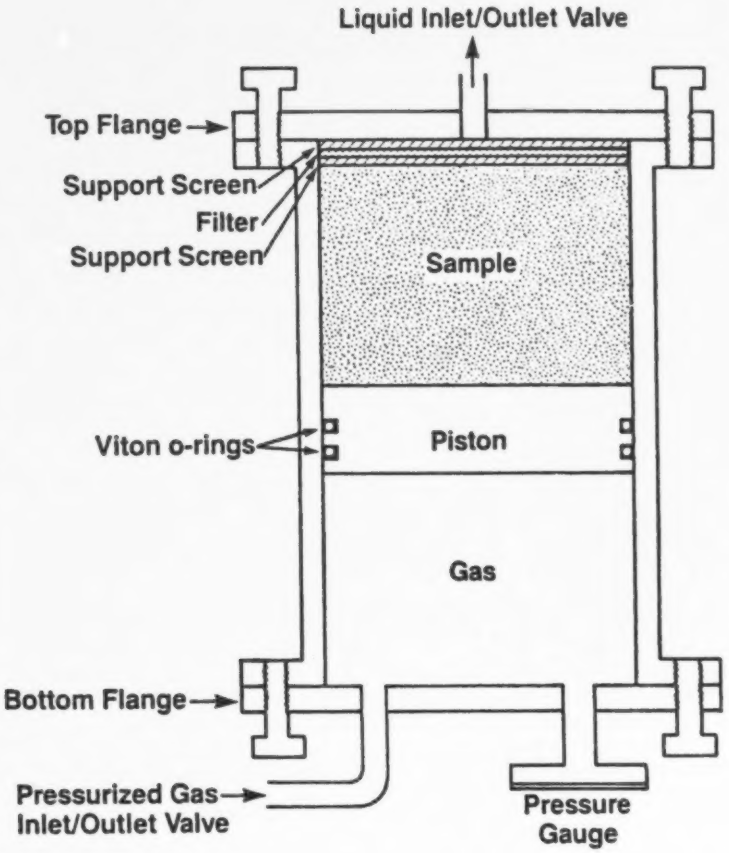

Liquid Inlet/Outlet Valve
Top Flange
Support Screen
Filter
Support Screen
Sample
Viton o-rings
Piston
Gas
Bottom Flange
Pressurized Gas Inlet/Outlet Valve
Pressure Gauge

Figure 3. Zero-headsapce extractor (ZHE).

TABLE 3. SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3740-ZHB, Gas Pressure Device
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	SDI P581 C5, Gas Pressure Device

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (See Table 3). Whereas the volatiles procedure (See Section 9.0) refers to pounds-per-square-inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel - When the waste is being evaluated for other than volatile contaminants, a 2-liter jar is used. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the contaminants to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices - It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE) - When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder - When the waste is evaluated for other than volatile compounds, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (See Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (Filter holders having an internal capacity of 1.5 L or greater and equipped to accommodate a 142 mm diameter filter are recommended). Vacuum filtration is recommended only for wastes with low solids content (<10 percent) and for highly granular liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

TABLE 4. SUITABLE FILTER HOLDERS[1]

Company	Location	Model	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm. 47 mm.
Micro Filtration Systems	Dublin, CA (415) 828-6010	302400	142 mm.
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm. 47 mm.

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that is is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic contaminants are of concern. The 142 mm size filter holder is recommended.

4.3.3 Materials of Construction - Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene, or polyvinyl chloride may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are constituents of concern.

4.4 Filters - Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-µm or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters - Any of the commonly available pH meters are acceptable.

4.6 ZHE Extract Collection Devices - TEDLAR® bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of non-aqueous liquid (i.e., <1 percent of total waste), the TEDLAR® bag should be used to collect and combine the initial liquid and solid extract. The syringe is not recommended in these cases.

4.6.2 If a waste contains a significant amount of non-aqueous initial liquid phase (i.e., >1 percent of total waste), the syringe or the TEDLAR bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant solid phase (is 100 percent liquid), either the TEDLAR bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices - Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (See Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance - Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

TABLE 5. SUITABLE FILTER MEDIA

Company	Location	Model	Pore Size
Millipore Corp.	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corp.	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7

5.0 REAGENTS

5.1 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the method detection limit of the analyte(s) of interest. For non-volatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.1.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.1.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5°C, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.2 Hydrochloric Acid (IN), HCl - made from ACS reagent grade.

5.3 Nitric Acid (1N), HNO3 - made from ACS reagent grade.

5.4 Sodium Hydroxide (1N), NaOH - made from ACS reagent grade.

5.5 Glacial Acetic Acid, HOAc - ACS reagent grade.

5.6 Extraction Fluid.

5.6.1 Extraction Fluid No. 1 - Add 5.7 mL glacial HOAc to 500 mL of the appropriate water (See Step 5.1), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

5.6.2 Extraction Fluid No. 2 - Dilute 5.7 mL glacial HOAc with ASTM Type II water (See Step 5.1) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.7 Analytical Standards - Prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 At least two separate representative samples of a waste shall be collected. If volatile organics are of concern, a third sample shall be collected. The first sample is used in several preliminary TCLP evaluations (e.g., to determine the percent solids of the waste; to determine if the waste contains less than 0.5 percent dry solids and thus is its own extract after filtration; to determine if the solid portion of the waste requires particle-size reduction; and to determine which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste). These preliminary evaluations are identified in Section 7.0. The second, and, if required, third samples are extracted using the TCLP non-volatile procedure (Section 8.0) and volatile procedure (Section 9.0), respectively.

6.3 Preservatives shall not be added to samples.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile contaminants, care shall be taken to minimize the loss of volatiles. Samples shall be taken and stored in a manner to prevent the loss of volatile contaminants.

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. If stored, even for a short period of time, storage shall be at 4°C, and samples for volatiles analysis shall not be allowed to come into contact with the atmosphere (i.e., no headspace). See Section 10.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PRELIMINARY EVALUATIONS

Perform the preliminary TCLP evaluations on a minimum 100-gram representative sample of waste. This sample (designated as the first sample in Step 6.2) will not actually undergo TCLP extraction. These preliminary evaluations include:

1. determination of the percent solids of the waste;

2. determination of whether the waste contains insignificant solids, and is therefore, its own extract after filtration;

3. determination of whether the solid portion of the waste requires particle size reduction, and

4. determination of which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste.

7.1 Preliminary Determination of Percent Solids - Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1 If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100 percent solids), proceed to Step 7.3.

7.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.1.3 through 7.1.9.

7.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.5 Weigh out a representative subsample of the waste (100 gram minimum) and record the weight.

7.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1 to 10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10-psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (See Step 7.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.1.5 or 7.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (step 7.1.9)}}{\text{Total weight of waste (Step 7.1.5 or 7.1.7)}} \times 100$$

7.2 Determination of Whether Waste is Liquid or has Insignificant Amounts of Solid Material - If the sample obviously has a significant amount of solid material, the solid phase must be subjected to extraction; proceed to Step 7.3 to determine if the waste requires particle-size reduction. Determine whether the waste is liquid or has insignificant amounts of solid material (which need not undergo extraction) as follows:

7.2.1 Remove the solid phase and filter from the filtration apparatus.

7.2.2 Dry the filter and solid phase at 100 ± 20.C until two successive weighings yield the same value within ± 1 percent. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry waste + filter) - tared weight of filter}}{\text{Initial weight of waste (Step 7.1.5 or 7.1.7)}} \times 100$$

7.2.4 If the percent dry solids is less than 0.5 percent, consult Step 6.2 and proceed to Section 8.0 if non-volatiles in the waste are of concern, and to Section 9.0 if volatiles are of interest. In this case, the waste, after filtration is defined as the TCLP extract. If the percent dry solids is greater than or equal to 0.5 percent, and if the non-volatile TCLP is to be performed, return to the beginning of this Section (7.0) with a new representative waste sample, so that it can be determined if particle-size reduction is necessary (Step 7.3), and so that the appropriate extraction fluid may be determined (Step 7.4) on a fresh portion of the solid phase of the waste. If only the volatile TCLP is to be performed, see the Note in Step 7.4.

7.3 Determination of Whether the Waste Requires Particle-Size Reduction (particle-size is reduced during this step) - Using the solid portion of the waste, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm [0.375 inch] standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken, see Step 9.6.

NOTE: Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended.

7.4 Determination of Appropriate Extraction Fluid - If the solid content of the waste is greater than or equal to 0.5 percent and if TCLP extraction for non-volatile constituents will take place (Section 8.0), perform the determination of the appropriate fluid (Step 5.6) to use for the non-volatiles extraction as follows.

NOTE: TCLP extraction for volatile constituents uses only extraction fluid No. 1 (Step 5.6.1). Therefore, if TCLP extraction for non-volatiles is not required, proceed to Section 9.0.

7.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle-size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500-mL beaker or Erlenmeyer flask.

7.4.2 Add 96.5 mL of reagent water (ASTM Type II) to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is $\leq$5.0, use extraction fluid No. 1. Proceed to Section 8.0.

7.4.3 If the pH from Step 7.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes.

7.4.4 Let the solution cool to room temperature and record the pH. If the pH is $\leq$5.0, use extraction fluid No. 1. If the pH is >5.0, use extraction fluid No. 2. Proceed to Section 8.0.

7.5 The sample of waste used for preliminary evaluations (Step 7.1 through 7.4) shall not be used any further. Other samples of the waste (See Step 6.2) shall be employed for the Section 8.0 and 9.0 extractions.

8.0 PROCEDURE WHEN VOLATILES ARE NOT INVOLVED

A minimum sample size of 100 grams (solid and liquid phases) is required. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

8.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e. is 100 percent solid, See Step 7.1), weigh out a representative subsample of the waste (100 gram minimum) and proceed to Step 8.9.

8.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in step 4.3.2 and is outlined in Steps 8.3 to 8.8.

8.3 Pre-weigh the container that will receive the filtrate.

8.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (See Step 4.4).

NOTE: Acid washed filters may be used for all non-volatile extractions even when metals are not of concern.

8.5 Weigh out a representative subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5 percent dry solids (Step 7.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5 percent dry solids (Steps 7.1 or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

8.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

8.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (See Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1 to 10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period) stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Step 8.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 8.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

8.9 If the waste contains <0.5 percent dry solids (See Step 7.2), proceed to Step 8.13. If the waste contains $\geq$0.5 percent dry solids (See Step 7.1 or 7.2), and if particle-size reduction of the solid was needed in Step 7.3, proceed to Step 8.10. If the waste as received passes a 9.5-mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 8.11.

8.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

8.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1)} \times \text{weight of waste filtered (Step 8.5 or 8.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (See Step 7.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e. temperature of room in which extraction takes place) shall be maintained at 22 ± 3°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

8.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 8.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (See Step 4.4) if evaluating the mobility of metals.

8.13 Prepare the TCLP extract as follows:

8.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.12 is defined as the TCLP extract. Proceed to Step 8.14.

8.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 8.12 with the initial liquid phase of the waste obtained in Step 8.7. This combined liquid is defined as the TCLP extract. Proceed to Step 8.14.

8.13.3 If the initial liquid phase of the waste, as obtained from Step 8.7, is not or may not be compatible with the filtered liquid resulting from Step 8.12, do not combine these liquids. Analyzes these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Step 8.14.

8.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis (metals aliquots must be acidified with nitric acid to pH <2, all other aliquots must be stored under refrigeration (4°C) until analyzed). The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals, other than mercury, shall be acid digested. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volumeweighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).

C_1 = The concentration of the contaminant of concern in the first phase (mg/L).

V_2 = The volume of the second phase (L).

C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

8.15 Compare the contaminant concentrations in the TCLP extract with the thresholds identified in the appropriate regulations. Refer to Section 10.0 for quality assurance requirements.

9.0 PROCEDURE WHEN VOLATILES ARE INVOLVED

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500-mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

9.1 Pre-weigh the (evacuated) filtrate collection container (See Step 4.6) and set aside. If using a TEDLAR bag, express all liquid from the ZHE device into the bag whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in 4.6.1 to 4.6.3.

9.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 9.0, Step 7.1 and/or 7.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

9.3 If the waste is 100 percent solid (See Step 7.1), weigh out a representative subsample (25 gram maximum) of the waste, record weight, and proceed to Step 9.5.

9.4 If the waste contains <0.5 percent dry solids (Step 7.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing ≥0.5 percent dry solids (Steps 7.1 and/or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

9.4.1 For wastes containing <5 percent solids (See Step 7.1), weigh out a representative 500-gram sample of waste and record the weight.

9.4.2 For wastes containing ≥5 percent solids (See Step 7.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of Waste to Charge ZHE} = \frac{25}{\text{\% solids (Step 7.1)}} \times 100$$

Weigh out a representative subsample of the waste of the appropriate size and record the weight.

9.5 If particle-size reduction of the solid portion of the waste was required in Step 7.3, proceed to Step 9.6. If particle-size reduction was not required in Step 7.3, proceed to Step 9.7.

9.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle-size as described in Step 7.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself.

If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

> NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 9.7.

9.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

9.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

> NOTE: If waste material (>1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 9.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (to flange) open, begin applying gentle pressure of 1 to 10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/ outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 percent solid (See Step 7.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Step 9.12.

9.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1 to 10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

9.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5 percent dry solids (See Step 7.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Step 9.15.

9.11 The liquid phase may now be either analyzed immediately (See Steps 9.13 through 9.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid number 1 to add to the ZHE as follows:

$$\text{Weight of Extraction Fluid} = \frac{20 \times \%\ \text{solids (Step 7.1)} \times \text{weight of waste filtered (Step 9.4 or 9.8)}}{100}$$

9.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid No. 1 is used in all cases (See Step 5.6).

9.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

9.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5 to 10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Repressurize the ZHE with 5 to 10 psi and check all ZHE fittings to ensure that they are closed.

9.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 22 ± 3°C during agitation.

9.13 Following the 18 ± 2-hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 9.9. All extract shall be filtered and collected if the TEDLAR bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (See Steps 4.6 and 9.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

9.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from step 9.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 9.13 and the initial liquid phase (Step 9.9) are collectively defined as the TCLP extract.

9.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to ± 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).

C_1 = The concentration of the contaminant of concern in the first phase (mg/L).

V_2 = The volume of the second phase (L).

C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

9.16 Compare the cortaminant concentrations in the TCLP extract with the thresholds identified in the appropriate regulations. Refer to Section 10.0 for quality assurance requirements.

10.0 QUALITY ASSURANCE REQUIREMENTS

10.1 Maintain all data, including quality assurance data, and keep it available for reference or inspection.

10.2 A minimum of one blank (extraction fluid No. 1) for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment are occurring.

10.3 For each analytical batch (up to twenty samples), it is recommended that a matrix spike be performed. Matrix spikes should be added after filtration of the TCLP extract and before preservation. (Matrix spikes should not be added prior to extraction of the sample). The purpose of the matrix spike is to monitor the adequacy of the analytical methods used on the TCLP extract and for determining if matrix interferences exist in analyte detection.

10.4 All quality control measures described in the appropriate analytical methods shall be followed.

10.5 The method of standard addition shall be employed for each metallic analyte if: 1) recovery of the compound from the TCLP extract is not between 80 and 120 percent, or 2) if the concentration of the constituent measured in the extract is within 20 percent of the appropriate regulatory threshold. If more than one extraction is being run on samples of the same waste (up to 20 samples), the method of standard addition need be applied only once and the percent recoveries applied to the remainder of the extractions.

10.6 Samples must undergo TCLP extraction within the following time period after sample collection: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days. Extraction of the solid portion of the waste should be initiated as soon as possible following initial solid/liquid separation. TCLP extracts shall be analyzed after generation and preservation within the following periods: Volatiles, 14 days; Semi-Volatiles, 40 days; Mercury, 28 days; and other Metals, 180 days.